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THE STRUCTURE OF REAL CRYSTALS

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In early days a crystal was defined as a solid bounded by plane faces of definite geometrical shapes; the angles between the faces were invariable, they did not change from one specimen to another of the same substance, although the *sizes* of the faces might change. Between the different faces on a crystal there could be symmetry relationships, and it was by means of these symmetry relationships that crystals were classified as being *triclinic hemihedral*, *orthorhombic enantiomorphic*, *cubic holohedral*, and so on. The optical perfection of some faces of some crystals grown naturally in the earth's crust, or grown in the laboratory, by slow cooling, slow evaporation or slow freezing from the melt, is so great that even the most skilled craftsman could hardly cut and polish faces as true.

In nature, however, perfect and complete crystals are rare. Recent investigations by Tolansky (*Proc. Roy. Soc.*, 1945, **A 184**, 41, 51, etc.) using a most sensitive multiple interferometry method, have revealed the existence of surface irregularities even on the most "perfect" crystal faces, the steps being only of the order of a few Angstrom units, and therefore microscopically invisible.

But crystals show more than regularity of shape. They show a certain regularity also of properties (leaving aside scalar properties such as temperature or density, which are uniform by nature). They are homogeneous (that is, their properties do not vary with translation in any direction); but only cubic crystals are isotropic (possessing certain properties which do not vary with rotation). The variation of physical properties, such as dielectric constant, coefficient of thermal expansion, thermal and electrical conductivities, refractive index, magnetic susceptibility, with direction, is of an orderly nature, however, even in anisotropic crystals, and is theoretically reproducible from one crystal to another of the same kind.

Yet even in this respect crystals may be, in fact, far from ideal. It is not easy, for example, to get consistent results for the thermal expansions of rochelle salt single crystals within the temperature range − 30° to + 25° C. (Ubbelohde and Woodward, *Proc. Roy. Soc.*, 1946, **A 185**, 453); while properties such as strength, breaking load, hardness, vary enormously from one crystal to another. Diamonds, since they belong to the cubic system, should be optically isotropic, but many are not. Of course it is easy to see that the presence of impurity and of strain may cause anisotropy or weakness. Large natural inclusions in a diamond may sometimes even cause spontaneous cleavage when temperature conditions change. Actually, however, lack of homogeneity can make crystals, particularly metal crystals, stronger than ideal crystals would be, by preventing glide from occurring as easily as it can do in single crystals; while twinning can cause the simulation of symmetry or of optical regularity higher than that which the crystal really

Even before the days of X-ray crystallography, it was believed that the peculiarities of shape and regularity of properties of crystals must be due to a regularity of the arrangement of atoms or molecules in the crystal. X-ray investigation confirmed this, and has given details of these arrangements for nearly all the elements and for hundreds, or even thousands, of compounds. It is now possible, therefore, to describe a crystal in terms of its atomic architecture, and to build a model showing how the plane faces are related to the internal structure. X-rays do not, however, show the arrangement of the atoms directly, as a microscope shows the structure of a beetle's eye. What is first obtained is the diffracting power of the crystal for X-rays under various conditions: crystal rotating, oscillating, stationary, etc.; and the atomic arrangement is deduced from this diffracting power, generally by making use of what is known as the reciprocal lattice method. Now it is very difficult, in fact, to say which best describes the *real* crystal: the crystallographic, physical and chemical description of the solid with plane faces that can be seen; a model of the atomic or molecular arrangement that can only be deduced; or the diffraction patterns which are the observable evidence of the internal arrangement. It is rather like deciding which is the real man, when one has a photograph, a description of character and ability, and a medical report. None of them is complete without the rest and all of them together are not really complete. They leave out of account that elusive thing, personality. Early X-ray crystallographers were satisfied when they had built a model with balls to represent atoms, or when

they could give the dimensions of the unit cell and the co-ordinates of the different atoms relative to the crystal axes. They knew, of course, that crystals were seldom, if ever, ideal; but lack of perfection was something to be corrected for rather than to be studied for its own sake. This also applied in the later stages of X-ray crystal studies, when the objective was a complete description, derived from a Fourier synthesis, of the electron density distribution. It still had to be assumed that the distribution was a strictly periodic one, and deviations from regularity, which resulted in a blurring of the picture, were ignored as far as possible.

What deviations from regularity actually exist?

There are boundary conditions; irregularities of crystal texture; static irregularities of structure which may be due to distortion, disorder or defect; and thermal vibration or translation of atoms.

First of all, then, there is the fact that crystals are not infinite; they have boundaries, and the conditions at or near the boundaries must differ from those in the body of the crystal. Not very much is yet known about surface conditions, although electron diffraction, electron microscopy and optical interferometry methods are beginning to give useful information. We can learn something also from the way in which crystals can grow on one another. For example, in the process of age-hardening of Al-Cu (and Al-Ag) alloys, studied by Preston (*J. Sci. Instr.*, 1941, **18**, 154) there is an intermediate stage in which a metastable form of $CuAl_2$ grows on the aluminium matrix; and the very existence of this form seems to arise from the fact that one of its main faces can "fit," not exactly but with relatively little strain, on one of the main faces of the cubic Al structure. Sometimes the habit (not the structure) of a crystal can be changed, as for example by growing it on another crystal as base, or by adding to the solution from which it crystallises a small quantity of some foreign substance which does not, however, enter the actual crystal. This kind of control of crystal habit has important commercial applications. Crystals of certain shapes can pack together conveniently, for transport, without consolidation and without grinding each other to powder. The toxicity of D.D.T. is found to depend very markedly on the size and shape of the D.D.T. crystals. Needle-shaped crystals of length 350 μ are twelve times as toxic as colloidal D.D.T. (McIntosh, *Nature*, 1946, **158**, 417). X-ray studies have shown that red and yellow Cu_2O are identical except for crystallite size. But red and yellow PbO have quite different structures.

Crystallite size and shape can both be measured, to a certain extent, by electron microscope studies, by low angle scattering of

X-rays, and by X-ray diffraction methods. In X-ray powder photographs, small crystallite size causes a broadening of the powder lines, the broadening varying with the line considered if the crystallites are not spherical. In rotation or fibre photographs it causes an extension of size of the diffraction spots. The powder method is used mainly for approximately spherical crystals, such as those of catalysts, whose sizes lie within the colloidal range, less than 100 A.U. linear dimensions. Elongated crystallites occur in many natural fibres, such as wool. In crystals of either of these two classes, catalysts or fibres, the relative amount of *surface* for a given weight of substance is a fundamental property. It may seem curious to speak of wool as crystalline when we remember the definition given at the beginning of this article, but our present definition of a crystalline substance is that it should have an atomic arrangement whose *time average* shows spatial periodicity in one, two or three dimensions over at least two or three "repeats." Even single crystals, although they may show excellent faces, are usually not "single" at all; they are a conglomerate of crystallites of linear dimensions 10^{-3} cm. or less. Sometimes these crystallites are parallel to each other, but discontinuous; sometimes they are disorientated by a few minutes or even degrees, although each crystallite may be perfectly regular in its own internal structure.

Not only size, then, but *arrangement* of the crystallites is important. In cotton hairs the component crystallites form a spiral structure, with their lengths inclined at a roughly constant angle to the fibre axis. Spiralling and other distortion of the crystallites often result in the drawing out of the diffraction spots on rotation or fibre photographs into arcs. Laue photographs of so-called "single" crystals often reveal spiralling, which in this case results in a tilting or focusing of the spots (Lonsdale, *Min. Mag.*, 1945, **27**, 112), but other conditions of texture or distortion give asterism, that is, radial extension of Laue spots. Orowan (*Nature*, 1941, **148**, 467) has described a way in which fragmentation may be distinguished from local lattice curvature by means of the shapes of spots on rotation photographs; but the whole question of crystal texture is one that is most difficult to study. Large-scale irregularities can be detected by ionisation spectrometer "sweep curves," as described by James (*Z. Kristallogr.*, 1934, **89**, 295) and Robinson (*Proc. Roy. Soc.*, 1933, **A 142**, 434), but it is always difficult to tell whether there is disorientation of small perfect crystallites, or an actual bending and distortion of crystal planes.

One curious consequence of crystal imperfection, however caused, was appreciated very early in the history of X-ray crystallography.

That is the fact that the total reflection from perfect crystals is much less, perhaps even thirty times less, than that from mosaic crystals or from the same weight of small individual crystallites. "Extinction," as it is called, is a measure of crystal perfection; it was carefully studied by early crystallographers in order that it might be possible to determine what part of the crystal diffraction of X-rays was due to the actual electronic scattering. Two kinds of extinction were recognised. Primary extinction occurs in crystals where perfection of structure extends over more than about 10^{-3} cm. linear dimensions and is due partly to the fact that the angular range of reflection is very small and partly to a destructive interference of multiply reflected and transmitted waves which are opposite in phase to each other, so that reflection is effectively confined to surface layers only. Secondary extinction occurs even in mosaic crystals, where the crystallites are 10^{-4} cm. or less in size, and is due to the fact that when reflection has already taken place in the upper layers of a crystal, the X-ray beam incident on the lower layers is reduced in intensity, and the total reflection from the lower layers is therefore decreased. But secondary extinction must vary with the *kind* of mosaic structure that exists. If the crystallites in a single crystal are parallel, though discontinuous, there will be internal multiple reflection that will redirect energy into the incident beam, but without the phase-relationships that cause destructive interference. In that case the secondary extinction is less than it would otherwise have been, particularly for strongly reflecting crystal planes. These differences of extinction can be studied by investigating not merely the X-ray reflections from single crystal planes, but also the X-ray absorption. If a *divergent* beam of X-rays is incident on a single crystal of suitable size, the pattern (Fig. 1, Plate I) recorded on a film on the opposite side of the crystal will consist of white lines on a grey background, the white (absorption) lines marking the directions where Bragg reflection has diverted energy from the incident divergent beam and has increased the effective absorption. The appearance of these divergent beam absorption photographs is quite different for crystals of the same substance but of different textures (Lonsdale, *Phil. Trans. Roy. Soc.*, in the press). This kind of study has also shown that variability of spacing, in single crystals of diamond, is small, even when there is marked distortion, resulting in variation of crystallite orientation. Differences of spacing are best revealed by the high angle reflections; if such differences exist, the reflection or absorption lines corresponding to high orders will be broader than those for low orders; this is not the case to any marked extent. Studies

of different diamonds have shown, however, that quite large differences of mean spacing, of the order of 1 in 10,000 (seven times as large as the experimental error) exist between one diamond and another, presumably due to the presence of impurities, small in quantity but well-distributed, which expand (or contract) the lattice as a whole. Such impurities, although they do not cause a marked variation of spacing within a single crystal, must certainly, however, introduce local irregularity or distortion.

Such local distortions will be even more widely spread in the case of various kinds of disordered and defect lattices, evidence for the existence of which has been gradually accumulating over the past fifteen years. In 1932 Barth and Posnjak (*Z. Kristallogr.*, **82,** 325) pointed out that in certain spinels, whose formula would ordinarily be written AB_2O_4, half of the B and all the A metal ions were randomly distributed in the cation positions which in normal spinels would be occupied by B ions alone. The correct way of writing the formula of such spinels would be $B(A,B)O_4$. This is one type of disordered structure in which all the atomic positions are filled but, in some cases, randomly filled. A random arrangement of this kind is, of course, almost inevitable in a mixed crystal of say (K,Na)Cl, where the metal ions need not be present in any simple ratio, and where they randomly occupy the cation positions in the rock-salt type of structure. But $Li_2Fe_2O_4$ and Li_2TiO_3 also each crystallise in a (not very stable) rock-salt lattice, the unit cell containing 4 metal and 4 oxygen atoms only. The arrangement of the metal ions must therefore be quite random, in spite of their simple numerical ratio and in spite of their different valencies; each cation surrounds itself by six O ions without being influenced by the metal ions lying beyond. Both these compounds can form mixed crystals, of the rock-salt type, with each other and with MgO, which also has the rock-salt structure. It seems to be rather a question of ionic *size* as to whether such random structures are possible or not. $NaBiS_2$ and $KBiS_2$ each have an averaged rock-salt structure, but $KFeS_2$ and $NaCrS_2$ have not (Boon, *Rec. Trav. Chim. Pays-Bas*, 1944, **63,** 32; Boon and MacGillavry, *ibid.*, 1942, **61,** 910).

	Li^+	Mg^{2+}	Fe^{3+}	Ti^{4+}	Na^+	Bi^{3+}	K^+	Cr^{3+}	O^{2-}	S^{2-}
Ionic radii . .	0·78	0·78	0·67	0·64	0·98	1·13	1·33	0·64	1·32	1·74

As the table shows, the difference in radii of K and Fe or of Na and Cr is large, evidently too large for the ions to be interchangeable. An increasing number of these random structures, some of them

quite complicated ones, are now being found. One of the most interesting is that of $Fe(CNCH_3)_6.Cl_2.3H_2O$, examined by Powell and Bartindale (*J. Chem. Soc.*, 1945, 799). Chemical analysis showed without doubt that there are 2 Cl atoms and 3 H_2O groups present in each molecule, but a direct Fourier synthesis showed the apparent presence of 2 H_2O and 3 Cl. Closer examination, however, made it clear that the " Cl " peaks are too low ; actually, they each correspond to ($\frac{2}{3}$Cl + $\frac{1}{3}H_2O$), because 2 Cl atoms and one H_2O group, which are approximately of the same size, are randomly distributed in three crystallographically equivalent positions.

Random or disordered structures are, of course, common in alloys composed of pairs of atoms (such as Ag and Au) which are of similar size, when they are cooled quickly from the melt ; although the most recent investigations of Guinier (*Proc. Phys. Soc. Lond.*, 1945, **57**, 310) indicate that *complete* disorder never exists, but that there is always a tendency for atoms of one kind to surround themselves by atoms of another kind (see also J. A. Wasastjerna, *Soc. Sci. Fenn. Comm. Phys.-Math.*, 1946, **13**, (5), 1).

Another sort of disordered structure, which must certainly introduce large local strain, is that in which some cation or anion positions are vacant, although the crystal as a whole is electrically neutral. The mineral pyrrhotite rarely has the exact composition FeS ; there is always a small excess of S, which can form up to 55·5 atomic per cent. of the compound. This is, in fact, due to the absence of some ferrous ions from the structure and the presence of a smaller number of ferric ions to maintain the electrical balance. The structure of γAl_2O_3 and γFe_2O_3 is even more extraordinary, for these two oxides can form structures of the spinel type, with 32 oxygen ions in the unit cell, but with an average of one out of every 9 cation positions vacant, giving (for γFe_2O_3) a statistical $21\frac{1}{3}$ ferric ions to occupy 24 metal sites. The result is that normal spinels can take up in solid solution any quantity of this form of Al_2O_3 or Fe_2O_3, forming mixed crystals in which some metal sites are vacant. Mixed crystals with some vacant sites must also result from the solution of $MgCl_2$ in LiCl, or of $CdCl_2$ in AgCl. Every Cd^{2+} ion that goes into the lattice leaves a vacant Ag position and, incidentally, enormously increases the electrical (ionic) conductivity. That electrolytic conduction occurs in ionic crystals at all must mean that ions can move through the lattice under the influence of an applied field, and this is due, in part at least, to the occasional existence of " holes " in the lattice resulting from the displacement of the ions that formerly occupied that space, as Dr. Bowen explained in his article on " Physical States of Aggregation " (SCIENCE PRO-

GRESS, 1946, **34**, 477). But these *accidental* holes are rare; even near to the melting-point the fraction of displaced atoms or ions is only 10^{-5}. The vacant sites which we are now discussing are an *integral part of the real structure* of the crystal. They exist because the number of available atoms is not sufficient to fill all the available equivalent positions at once. Examples can be multiplied. The low temperature form of Ag_2HgI_4, which is yellow, becomes cubic at about 50° C. and turns red. In the cubic form there are two Ag atoms and one Hg atom statistically occupying 4 equivalent positions in the unit cell; on the average one out of every 4 cation positions is vacant. The high temperature form of AgI is also a defect structure, with an ionic conductivity which is higher even than that of molten AgI. In fact, although the I positions form a comparatively rigid body-centred cubic lattice, the Ag atoms are so mobile that they may be said to exist as an interstitial liquid within the framework of easily deformed I atoms.

Even in structures, such as NaCl itself, where all the atomic sites are filled, and filled in an orderly fashion, a certain randomness of structure is introduced by the thermal vibrations of the individual atoms about their mean, regular positions. Early X-ray crystallographers were able to measure the average amplitudes of vibration at different temperatures and they found that, in general, metal atoms are more loosely bound in the lattice than the anions (halogen, oxygen, etc.) which interleave them. They could also show that even at absolute zero there was a probable displacement of atoms from their average positions (zero-point energy). More recently, in carrying out the analysis of crystal structures, it has been found that only by the assumption of an *anisotropic* heat vibration of atoms or molecules can agreement be obtained between calculated and observed intensities of reflection in certain cases. This applied, for example, to the structure of melamine, in which flat molecules vibrate strongly in a direction normal to their plane (Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737).

During the last seven years, the study of the diffuse X-ray scattering outside the Bragg reflecting positions has made it possible to measure not just the average amplitudes of vibration, but the actual amplitudes in different directions for vibrations of different polarisation and frequency. The study of these thermal vibrations is important, not only because they are universal, but also because they give information about the forces binding the atoms or molecules together. If the forces between the atoms are strong and isotropic, as in diamond or tungsten, then the thermal vibrations will be small and isotropic also. The forces between the atoms are

themselves related to the elastic constants of the crystal as a whole, that is, to the ratio of stress/strain for different kinds of strain. In soft metals such as Na, Li or Pb the elastic constants are small, that is, a small force will produce large distortion ; the interatomic forces are therefore small and the thermal vibrations large, and not only large but extremely anisotropic. In some directions, in fact, the vibrations are so large that atoms can easily " break loose " and wander through the lattice. Hence the markedly temperature-dependent self-diffusion phenomena in Pb, which can be traced by labelling certain atoms with radio-activity, and hence also the diffusion of one metal through another that takes place when the two are placed in close contact. A recent example of such diffusion is found in the carburisation of tungsten, which apparently takes place not by diffusion of carbon along the grain boundaries, but by diffusion of carbon atoms through the tungsten-carbide lattice to the tungsten–tungsten-carbide interface (Pirani and Sandor, *J. Coal Research*, 1946, June, p. 54).

The diffuse X-ray scattering caused by the thermal vibrations is best studied either by means of the ionisation spectrometer, or by well-exposed X-ray photographs of stationary single crystals taken with radiation containing a strong monochromatic component. Superimposed on the ordinary Laue photograph of sharp spots given by the white radiation is a diffuse pattern having the same symmetry, but otherwise very dissimilar, given by the characteristic radiation. In order to study this diffuse pattern in more detail, monochromatic radiation can be used, eliminating the Laue pattern altogether. Just as the *average arrangement* of atoms can be deduced from the ordinary diffraction patterns, so the *vibrations* of the atoms can be deduced from the diffuse patterns. This is only possible because the thermal vibrations are so slow relative to the X-ray frequencies that to the incident X-rays the structure is an ordered arrangement with, superimposed upon it, a large number of stationary waves (the plane waves into which the atomic displacements can be resolved). A single " diffuse photograph " takes account of only a few of these waves at a time, but by suitably adjusting the crystal orientation it is possible to study just those sets of waves that are most interesting. Quite general considerations of lattice forces tell us that in layer structures, such as graphite or hexamethylbenzene, the atomic movements will take place most easily in directions *normal* to the layer planes. They can be resolved either into longitudinal vibrations travelling normal to the layer planes or into transverse vibrations travelling parallel to the layer planes or into waves, neither longitudinal nor transverse, travelling in other direc-

tions. These large atomic movements give rise to a large, intense, elliptically shaped diffuse reflection in the neighbourhood of the Bragg reflection from the layer plane (Fig. 2, Plate I).

In chain structures, on the other hand, the atoms cannot move along the chain direction except with great difficulty. It is known (Muller, *Proc. Roy. Soc.*, 1941, **A 178,** 227) that the compressibility of long-chain paraffins along the chain length is negligibly small. This means that longitudinal vibrations travelling along the length of the chain are forbidden (and *some* transverse vibrations travelling perpendicular to the chain length also). The diffuse scattering associated with planes normal to the chain length takes the form of long, thin streaks (Fig. 3, Plate II). Jahn (*Proc. Roy. Soc.*, 1942, **A 179,** 320) has calculated, in an easily applied form, the relationship between the shape of the diffuse scattering regions and the elastic constants of cubic crystals, and his formula has given excellent agreement for such crystals as KCl, NaCl, metallic Na, Li, Pb, W. The kind of thermal vibrations that take place in complex structures, however, include not only those that are controlled by the quasi-elastic forces within the lattice, but also vibrations (usually, but not always of small amplitude) in which groups of atoms rhythmically alter their configuration in the lattice framework. Lely and Bijvoet (*Rec. Trav. Chim. Pays-Bas*, 1944, **63,** 39) have shown, for example, that the CN groups in NH_4CN oscillate in the diagonal planes of the tetragonal structure. Since the high-temperature, cubic forms of NaCN, KCN, RbCN and CsCn all have very high symmetry (Lely, *Thesis*, Utrecht, 1942), the first three having structures of the NaCl and the last of the CsCl-type, it follows that the CN groups must have the same symmetry as the Cl ion. This is possible either by isotropic *rotation* of these groups, or by *statistical distribution* over a number of preferred positions (or over every possible orientation). It is very tempting to assume that it must be a rotation, which could be the final result of an oscillation of greater and greater amplitude. In some cases there almost certainly is such a rotation, but the evidence for the onset of rotation comes rather from changes in physical properties than from a unique interpretation of X-ray intensities. Zernike (*Ned. Tijdschr. Natuurkund.*, 1941, **8**, 66) has pointed out that in the case of NH_4Cl the right value of the entropy is obtained if it is supposed that at the transition point there is an order-disorder change in the orientation of the revolving NH_4 groups. Perdok (*Thesis*, Groningen, 1942) believes the same to be true of the transitions of the organic crystal $C(SCH_3)_4$, which has three modifications, a piezo-electric tetragonal form I, stable below 23·2° C.; an apparently body-centred, centro-

FIG. 1.—Divergent X-ray beam pattern of diamond: CuK radiation (positive reproduction).

FIG. 2.—Hexamethylbenzene: Laue photograph with radiation from Cu target. The very large intense diffuse spot comes from vibrations of the layer plane.

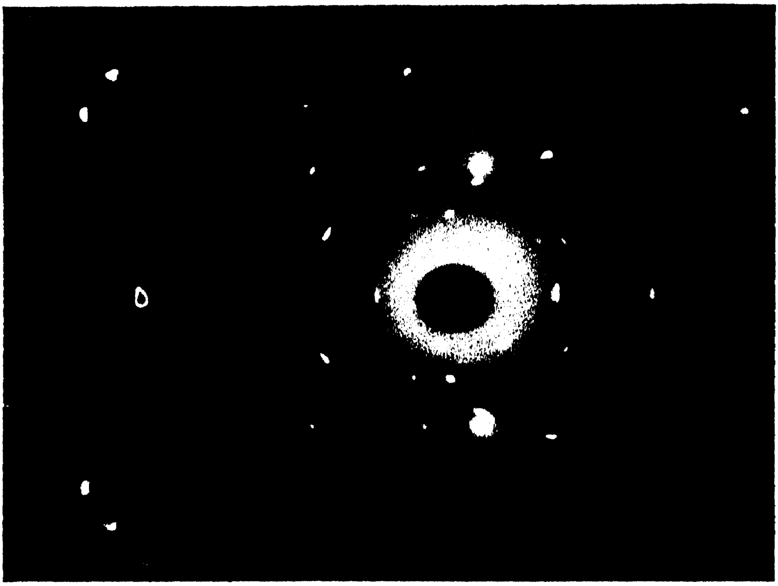

FIG. 3.—Sorbic acid: Laue photograph with radiation from a Cu target. The streaky diffuse spots are from planes nearly normal to the chain direction.

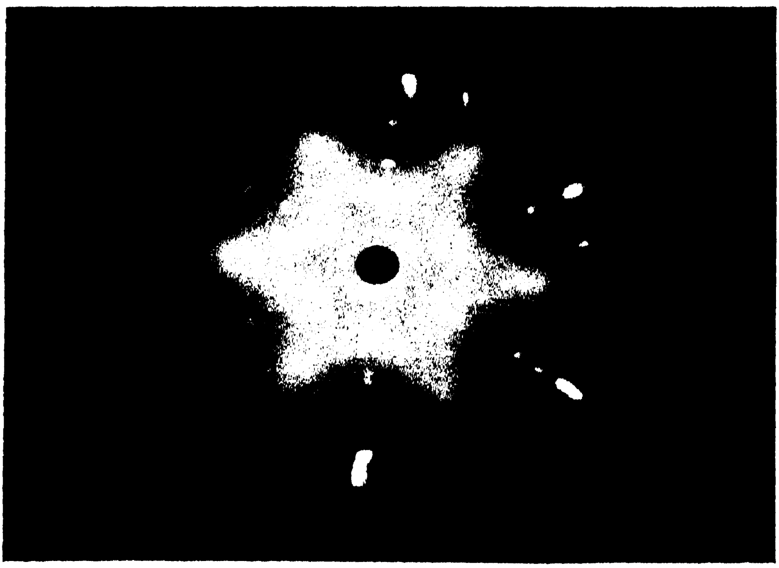

FIG. 4.—Ice, near 0° C.: Laue photograph with radiation from a Cu target.

symmetrical tetragonal form II, stable between 23·2° and 45·5° C.; and a body-centred cubic form III, stable from 45·5° C. to the melting-point, 65·7° C. He suggests that in form II the body-centring and centro-symmetry are both *simulated* by the statistical co-operation of a large number of unit cells, and shows that although both in II and III different molecular configurations must co-exist, there would be steric hindrance of an isotropic rotation of the molecules. Both these modifications are so plastic that although they give crystalline X-ray diffraction, they behave in some respects almost like liquids. There must be large thermal vibration, but this consists in a concerted jump of atoms from one preferred molecular orientation to another.

It is interesting to find that Pauling (*Nature of the Chemical Bond*, 1945, pp. 302–3), from entropy considerations, postulates that in ice there is not one molecular arrangement (which would mean the existence of a larger unit cell than that found by X-rays, which can only place the oxygen atoms) but a continual changing from one molecular configuration to another of equal energy, so that the unit cell of ice is *statistically* smaller than it would be if instantaneously isolated. The diffuse scattering of X-rays by ice is remarkable (Fig. 4, Plate II); it is certainly of thermal origin, for it disappears at low temperatures, but it cannot be explained simply in terms of the elastic constants of the crystal, and it may well be associated with the changes of molecular configuration indicated by the magnitude of the entropy (Lonsdale, *Nature*, 1946, **158**, 582).

Certain kinds of diffuse or non-Laue scattering, however, are not due to thermal vibration, but to some static periodicity in the structure. An example of this occurs during the heat-treatment of the alloy of approximate composition Cu_4FeNi_3, where at one stage there is an approximately sinusoidal variation of lattice spacing (Daniel and Lipson, *Proc. Roy. Soc.*, 1943, **A 181**, 368). Other X-ray evidence shows that in some structures, such as that of hexagonal Co, "mistakes" occur in the pattern in an approximately regular way, the structure being cubic instead of hexagonal for two or three planes in every ten or so; while graphite from many sources is found to contain a fairly uniform 14 per cent. of a different graphite modification as well as some 6 per cent. of a random arrangement of graphite layers. There are differences in certain physical properties (*e.g.* infra-red and ultra-violet absorption) as between some diamonds and others which, although associated with differences of texture, may also have some further structural origin which is not yet fully understood. The structure of real crystals almost certainly introduces many such problems for future investigation.

CHARACTERISTICS OF INSTINCTIVE BEHAVIOUR AS ILLUSTRATED BY THE SCARABÆIDÆ

By E. S. RUSSELL, O.B.E., D.Sc., F.L.S.

In order to make clear the main characteristics of instinctive behaviour I propose to take as a typical example the behaviour of the dung beetles of the genus *Scarabæus*. Their behaviour has been very fully and carefully observed, first by Fabre over a period of nearly forty years, and later by R. Heymons and H. von Lengerken (1929), who have added to, corrected, but in the main confirmed Fabre's results.

The scarab is diurnal in its activity, a creature of warmth and the south, at its liveliest in the hot sun and not occurring in colder climates. In the evening it goes to ground, not to emerge again till the morning warms up. It is primarily the scent of dung that rouses it to activity. Fabre describes vividly how the deposit of mule or sheep dung attracts to it all the scarabs in the vicinity, both those that are wandering around, and those that are buried in the sand near by. Only the scent of dung, perceived through the lamellated antennæ and, when near, through the maxillary palps, arouses the attention of the scarabs and provokes a search for this their exclusive food. They seek it with widely spread antennæ and when close go straight towards it. The smell of dung is, in fact, the one sensory perception that has food meaning or food "valence" for the dung-beetles in general. Our common *Geotrupes* behaves just like *Scarabæus*, scenting the breeze for a whiff of dung. To leeward of the dung it may smell it even 4 metres away; to windward it must be within about 50 cm. to perceive the smell (Warnke, 1931). It has been shown by Warnke that ammonia, skatol and indol, in that order, exercise a similar attraction to dung, of which they are, of course, constituents.

In the South of France and in Italy, where the observations of Fabre and the two German investigators were made, the scarabs utilise for food the dung of various, chiefly herbivorous, mammals—sheep, cow, horse, mule and others; even human excrement is

used. According to Heymons and von Lengerken sheep dung is the favourite, especially when fresh and moist. It is characteristic of the scarabs that they do not, or very rarely, eat the dung on the spot, though they may suck moisture from it. Their instinctive drive is to make it up into balls which they hastily roll away and bury. By so doing they act as efficient scavengers; the sanitary value of their operations in the crowded lands of the East has been especially emphasised by Hingston (1923).

The process of shaping the ball is a very interesting one. The ball does not owe its spherical shape to the fact that it is trundled for some considerable distance over the ground; it is moulded into a sphere on the spot, before it is moved. Two methods are employed according as the material is sheep dung or cow dung. With the first, a pellet of dung is seized and held throughout the whole operation, the beetle pulls towards it another pellet, splits off a piece and moulds it to the first, working the whole mass into a sphere. This process is repeated several times, so that the final product is a large ball containing in its centre the original pellet, surrounded by concentric layers of dung derived from other pellets and moulded over the first. The ball is not rotated during these manipulations; it is rounded and smoothed off below by pushing the head in from all sides.

If the ball is made from a cow pat, the scarab proceeds in a different way. Delving in with its head and scratching out with its fore legs, it moulds near the edge of the pat a hemisphere of dung, surrounded by a circular rim. It then cuts in under and all round the half-formed sphere, using its wedge-like head, so completing the sphere, and finally cutting it free from the pat. The ball is completely shaped before it is rolled away. In addition to the wedge-shaped head, Nature has provided the tools for the job of rounding off the ball in the specialised shape and structure of the middle and hind pairs of legs. The latter, particularly, are very long and curved. In both, but especially in the hind pair, the femur has a sharp edge on its posterior margin, hollowed out in a flat curve. This acts as a scraper, while the legs move over and around the surface of the growing ball. Each pair of legs may be likened to a pair of callipers with bent arms, and when they are extended they cover a hemispherical space of a definite size. It is this natural span that normally determines the size of the ball, for when the growth of the ball has stretched its legs to their full extent the beetle reaches the normal terminus or end-state of its labours and ceases its modelling work. Each different species has its own characteristic mean size of ball, corresponding to the span

of its legs. But circumstances or, better expressed, the "situation," may bring it about that the scarab rests content with a smaller ball than normal or even one that is irregularly shaped. This is liable to happen if there are many competitors working near by, or if the dung is hard and dry. Sometimes they will roll away a single pellet of sheep's dung, or a lump composed of a number of pellets, without moulding them into a ball. In their collecting they always give the impression of haste, as if to get their supply safely away as soon as possible from their neighbours. The dominating impulse is to move a supply of dung away from the heap and bury it some distance off. Normally and typically the dung is first moulded into a ball, which can be readily rolled away, but on occasion they may move away and bury even a shapeless piece of dried dung. An instance is described by Heymons and von Lengerken (pp. 536–7). A scarab, coming across a small piece of dry dung that could not be shaped into a ball, tried hard to remove it, propelling it a little way, using not only its hind legs in the usual manner but also pushing it with its head and finally burying it at no great distance. There is, it will be seen, a fair amount of variation of the rolling and burying routine, in response to varying circumstance.

The biological purposes served by the hasty transport and burying of the ball appear to be its rescue from the competing dung beetles of several kinds which swarm to the feast, and the protection of the ball from drying up in the hot sun.

In rolling the food ball away for future consumption the scarab, which may be either a male or a female, normally progresses backwards, propelling the ball along the ground by strokes delivered by its mid and hind legs. It usually buries the ball fairly near by, but may go as far as 8–15 metres before interring it. In its course it often comes up against obstacles and shows great persistence in trying to overcome them, working at the task for hours. If the ball gets stuck in vegetation the scarab may get under it and heave; if the ball is up against an impassable obstacle or falls into a hole from which it cannot be retrieved, the beetle may bury it where it lies. Scarabs in a terrarium try for hours to push the ball through the glass wall—an obstacle of which they have no experience in natural conditions. In general, according to Heymons and von Lengerken, *Scarabæus*, while persistent in its efforts, shows little understanding of the obstacle-situations which it encounters, and its success in circumventing them is largely a matter of chance. Both Fabre and Hingston (1928), however, have shown that *Scarabæus* and the allied genus *Gymnopleurus* can sometimes cope effect-

ively with unusual difficulties, as when the experimenter pins down their ball to the ground or suspends it just above their head. It is clear that the dung beetles show that important characteristic of behaviour which Lloyd Morgan called "persistency with varied effort," and to which Stout (1913) often refers in his masterly account of instinct from the psychological point of view.

Of *Gymnopleurus*, which is also a roller of balls, Hingston (1923) in India has made the interesting observation that they maintain unswervingly a constant direction in moving their ball away from the source of dung; each beetle, or more usually pair of beetles, persists in the direction in which it has set out, and if diverted from its course by the observer reverts unerringly to it. The result appears to be a maximal radial dispersion of the balls. While trundling its ball away, the scarab is frequently attacked by one of its own kind, which tries to take possession of the ball. Fights arise only in this way, and they take place only between beetles of the same sex, never between a male and a female. When approached by another scarab, the owner of the ball, holding on to it, smells the oncomer with its antennæ, especially at the dorsal integument in front of the mesothorax, and if it is of the same sex fights and, if possible, repels it. Sex is recognised by smell. If a female rolling a ball is approached by a male she recognises him as such and leaves the ball for him to roll, following close behind it. A female finding a male trundling a ball follows him at a distance of 2–3 cm.; he may stop and smell at her. Sometimes she sits on the ball, or she may walk forward holding on to it, appearing thus to help him. But according to Heymons and von Lengerken there is little or no mutual aid between the pair. It is the ball that the female is interested in, for if it is taken from him she ceases to follow; if the male is removed, the female takes possession of, and trundles, the ball. The dung sphere is the only bond between them, while they are engaged in food-getting activities.

Scarabæus does not know "its own" ball and will readily accept any other's, even if it be of a different size from its own. The ball is recognised solely by its smell. The beetle will accept balls made of other material, provided they smell of dung. For example, Heymons and von Lengerken found that while the scarab would pay no attention to suitably sized balls composed of dried fragments of *Posidonia* (a marine plant allied to *Zostera* or eel-grass), if these balls were smeared with fresh dung the beetle would roll them away and bury them. The scarab might stop on the way and smell the ball all over until it came across the dung smear, when it would resume its task. Leaden bullets sewn up in cloth and smeared

with dung were also accepted and rolled away, with difficulty; sometimes they were buried. A chestnut which had been in contact with dung was treated in the same way, and so were little pieces of wood similarly contaminated. The beetles naturally had great difficulty in rolling the bits of wood, and sometimes used the alternative method of shoving them along with their head—as did the beetle that tackled a piece of dried dung (p. 14 above).

While the burying of the ball can be carried out independently by a single male or female, it is usual for a pair to be concerned, when the male does the digging, while the female sits on the ball or rests near by. If the female is removed, the male pays no attention but goes on burying. If the male is taken away, the female takes charge of the ball and buries it either on the spot or some distance away. If the ball is removed, male and female go off separately to look for more dung. The bond between male and female is therefore very slight, and it is not individual, any male serving as temporary partner for any female.

There are two methods of burying the ball; either a hole is dug alongside and the ball rolled into it, or the soil is excavated directly below it so that it sinks into the burrow. The completed burrow is a curved tube which may extend a considerable distance below ground. The dung ball is thus kept fresh and moist, and, according to Heymons and von Lengerken, free from fungal growths. After the ball is buried, it is eaten up by its owner or owners. Such in brief is the story of the food-getting and food-storing activities of *Scarabæus*.

But dung balls are also made and buried for another biological purpose, the provision of food for the larva. These balls look exactly the same as the food balls, but they are prepared, rolled away and buried by the female alone. (They do *not* contain an egg, as is sometimes stated by earlier writers, including Stout.) They are made of sheep dung exclusively, if this is available. The burrows constructed for their reception differ from the food burrow in that the female hollows out at the bottom a large smooth-walled chamber, in which she reshapes the ball into a pear-shaped structure destined to receive her egg and to provide nutriment for the developing larva. As already indicated, the "pear" is normally composed of sheep dung, but this is not absolutely essential, for it has been noted by Heymons and von Lengerken (p. 585) that a female *S. laticollis*, having at her disposal only cow dung, constructed the larval pear of this material and the larva developed successfully.

The construction of the pear has been described by Fabre (V). Sometimes the female dispenses with the shaping of a ball and buries

on the spot a mass of soft sheep's dung, constructing a brood chamber and shaping the pear directly from the shapeless heap. Normally, however, the pear is modelled in the brood chamber from the ball, retaining on its surface the sand and earth which the ball has picked up while being rolled over the ground. Occasionally the female breaks up the ball into fragments and refashions the pear from these, when the pear has a smooth surface. The pear at first is spherical, then the female hollows out on top a shallow crater surrounded by a turned-over rim. The rim is later extended and closed in to form the narrow end of the pear, enclosing a small chamber in which the egg has already been laid. The wall of the egg-chamber is carefully smoothed; the large egg hangs from the top, which has been closed by a rather loosely constructed stopper, probably allowing some access of air. The kneaded outer surface of the pear is hard, forming a sort of shell, which protects the inner mass of dung from drying up. The completed pear, which always stands vertically and does not lie on its side, as Fabre supposed, bears a curious resemblance, functionally, to the egg of a bird, as Fabre was not slow to point out. "The pear of Scarabæus," he wrote, "can be compared with a hen's egg. Its shell is the hardened outer layer which prevents too rapid desiccation; its nutritive store, its yellow or yolk, is the noble ball protected by its rind; its air chamber the terminal cell, the nest in which lies the egg bathed all round by air" (V, p. 40).

The female never eats any part of the pear, and when she has finished making it she leaves the burrow and collects material for another pear. The female is persistent in her task of making the burrow and provisioning it. Four times Fabre destroyed the burrow destined for the pear, and four times she re-made it, re-burying the ball of dung or the half-formed pear. But when she has completed her work and laid her egg, the pear loses all meaning or valence for her; if it is exhumed and laid beside her she pays no attention to it but departs. The immediate goal or terminus of her work has been reached and she passes on to the next task. As Fabre aptly puts it, speaking of instinct in general, "the work to be done is everything, the work done no longer exists" (V, p. 102).

Scarabæus lays only a few (about 6) eggs, which in *S. sacer* measure on the average $8{\cdot}2 \times 4{\cdot}7$ mm. They are provisioned with yolk through physiological means, and, as we have seen, a further supply of food is provided by the instinctive activity of the mother, which the emerging larva finds at its door. The larva when it is hatched begins to feed on this rich store, and works its way steadily downwards until it has devoured all the dung within the hardened

rind, replacing it gradually with its own abundant excrement. It has the curious and useful habit of plastering up cracks or holes in the surface of the pear, whether these are caused by small dung beetles (*Onthophagus* or *Aphodius*) which have remained hidden in the dung, or gaps produced artificially by the experimenter. First it reconnoitres the hole with its head, then turns round and applies with its trowel-like hind end its own excrement to the edges and gradually cements up the hole. It can mend quite large holes, such for instance as are made by cutting off the pointed end of the pear. This repair work serves the useful purpose of preventing the contents of the pear from drying up, a danger which is always present during the summer months when larval and nymphal development is proceeding and to which the developing scarab often succumbs.

For emergence the nymph has to await the autumn rains of the South, which soften the ground and the hardened walls of the pear and permit the fully formed beetle to struggle up to the surface. The beetle may be ready to emerge in August, but usually has to await the rains that come at the end of September. When their free life begins they soon start to make and roll their food-balls, doing this perfectly from the first go off. So the cycle of behaviour comes full circle again.

This brief account of the behaviour cycle in *Scarabæus* enables us to form some idea of the essential characteristics of instinctive behaviour, both psychological and biological. We may note first the extreme simplicity and specialisation of the psychological activities involved. The adult scarab seeking food has the specialised "disposition" to pay attention to one specific scent only, that of dung, and to carry out a specific series of actions, comprising the moulding of a ball of dung, its transport and inhumation in a burrow. This perception-action disposition is inborn, and owes nothing to previous experience or learning; it appears at a definite stage of the life-cycle, ready to function. The scent of dung to which the scarab is predisposed to attend is normally adequate as indicative of the proper material from which to mould its balls, though in exceptional circumstances it may lead the scarab astray, as when it rolls and buries objects that are merely smeared with dung.

The course of action which the smell of dung excites is fairly stereotyped, but it is capable of modification according to the sensed or perceived situation. Thus the process of ball-making may be omitted or abridged, if the dung is too hard or competitors are too numerous. But the general formula or action is adhered to —removal of a portion of dung, usually in the shape of a ball, and its burial some way off. It is important to note that this course of

action is actively pursued till its successive goals are reached; the scarab persists in its work till the ball is made; it struggles to roll the ball over or round obstacles; its action is persistent with varied effort. This is an important characteristic of all behaviour, and it implies psychological factors.

It is often said that instinctive behaviour is blind, that the instinctive animal has no foreknowledge at all of the goal to which its actions are directed. There is a great deal of truth in this assertion. We have no reason to think that the scarab has a prior notion of what it is about in making and rolling its food-ball, still less a definite plan of action thought out beforehand. Nor can we suppose that in selecting special material for its larval pear, moulding it into a ball, constructing a special brood chamber and therein forming the pear so nicely adapted for the welfare of the larva, the female has in mind the biological purpose of her acts, which is the provision of suitable conditions for the development of her offspring—of which she can have no knowledge. It is sufficient to suppose that she has an inborn and specific impulse or drive to carry out certain acts in a certain order, without knowledge of the ultimate end or purpose of these actions. But it would be a mistake to think that her actions are completely blind, automatic and mechanical. There must be some forward-looking element in her behaviour, pointing towards the immediate goal, terminus or end-state of the action actually in progress; there must also be some consciousness, however dim, that her action has, or has not, reached its immediate goal; otherwise it would be impossible to explain why her action shows persistency till the goal is reached and then ceases.

But the dung beetle's behaviour is certainly not purposive in the human sense. The late Prof. G. F. Stout, in his analysis of instinct from the psychological point of view (1913), treats instinct as a form of perceptual process, thus marking it off as being on a lower level than the ideational and overtly purposive activity characteristic of man, and of man alone. This is a fundamental and generally accepted point, of crucial importance for the proper interpretation of animal behaviour. "The vast interval," he writes, "which separates human achievements, so far as they depend on human intelligence, from animal achievements, as far as they depend on animal intelligence, is connected with the distinction between perceptual and ideational process. Animal activities are, in the main, either purely perceptual, or, in so far as they involve ideas, these ideas only serve to prompt and guide an action in its actual execution. On the other hand, man constructs 'in his head,' by means of trains of ideas, schemes of action before he begins to carry

them out. He can cross a bridge ideally before he comes to it actually" (pp. 387–8). The contrast between animal and human behaviour is essentially that between impulsive or hormic behaviour guided by immediate perception and behaviour guided by ideas which are goals of action. Animals are in the main creatures of impulse.

Furthermore, behaviour on the perceptual level is always "purely and immediately practical in its operation . . . The theoretical question Why? has no existence for the merely perceptual consciousness" (p. 447). The instinctive animal "knows how" to act in a given normal situation, it does not know why it should so act. Its "knowledge" is practical—and effective—it is not theoretical. As Spaier (1930) aptly puts it, instinctive behaviour is a matter of "savoir-faire" not of "connaissance." Animal behaviour therefore should not be interpreted in terms of conscious purpose, of planned and foresightful action, such as human beings carry out; to do so is to fall into a gross anthropomorphic error. But much of our own behaviour, as for instance in playing tennis or dodging the traffic, takes place on the perceptual plane of direct "knowing-doing," and thus gives us an insight into the nature of perceptual process, of which instinctive behaviour is a form. Animals live a life of immediacy and impulse to which the non-intellectual part of our own experience as acting subjects gives us a valuable clue.

It is worth while noting that behaviour on the perceptual level, which is normally directive towards a biologically useful end-state, without explicit foreknowledge of it as end, is the rule in Nature, and consciously purposive action the exception, for all animals exhibit this form of behaviour, and only man rises to the ideational or conceptual level, and that not consistently or continuously. Furthermore, directiveness towards biological ends is characteristic of organic activities in general (Russell, 1945) and is basic to behaviour at both levels.

Regarded from a biological point of view, the behaviour of the scarabs is clearly directive towards goals related to the biological ends of self-maintenance, reproduction and development. Guided by a specific scent, the scarab seeks out for nourishment the food which is suitable to it, protecting it from desiccation by rolling it away and burying it; it recognises its mate by smell and performs the necessary act of copulation; it amasses food for the nourishment of its descendants, stores it in a burrow in a shape convenient for the hatching larva, continuing thus by behavioural means the cellular activities which have produced and provisioned the egg;

the growing larva eats the food provided for it, conserving it by repairing breaches in the wall of its domicile by the use of its own excrement. All these things the scarab does without knowledge of the biological purpose of its acts ; its behaviour is directive, like the morphogenetic and physiological activities of its cells, but none of these activities is purposive in the psychological sense. Its behaviour is integrated with, and forms an essential link in, the cycle of activities which constitute its life.

We have noted that the behaviour of *Scarabæus* is highly specialised both on the perceptive and the executive side. Biologically regarded, this behavioural specialisation is just one part or aspect of the integral specialisation in form and function of the scarab as a living whole. *Scarabæus* is essentially a diurnal Lamellicorn beetle which utilises dung in a particular way, adjusted to the climatic conditions in which it lives. Its bodily structure is related closely to its manner of behaviour. I have mentioned its wedge-shaped head, and the combined callipers and scrapers formed by its middle and hind legs, which facilitate the moulding of the ball ; to which it may be added that the fore legs are efficient excavating tools. Internal organisation also is related to the dung-eating habit. Dung is not a very nutritious substance, having passed already through one alimentary canal ; great quantities of it are therefore required for a meal. Fabre found that *Scarabæus* would eat steadily for at least 12 hours, consuming in that time about its own volume of dung, and producing a fæcal cord nearly 3 metres in length (V, pp. 24–5). In correlation with the great amount that has to be ingested and dealt with, the dung-beetles in general have an exceptionally long intestine. According to Henneguy (1904, p. 68), the length of the digestive tube in coprophagous Lamellicorns is on the average 10·19 times that of the body, as against 3·7 times in phytophagous members of the group.

The coprophagous Lamellicorns are a very extensive and widely distributed family, comprising no less than 17 sub-families (Kolbe, 1905), several of which are very rich in species. A few of them live on and store carrion, and one or two feed on and store leaves and shoots, but the great majority depend entirely on dung for food for themselves and their offspring. They show a considerable diversity in the way in which they utilise dung for these two purposes, being specialised in their behaviour in several different directions. Some small forms, such as the Troginæ and the Aphodiinæ, simply feed on the dung as they find it, and lay their eggs in it, making only this general provision for their offspring. *Onthophagus* also feeds directly on the dung, without storing it for future con-

sumption, but it makes quite an elaborate burrow directly under the dung, provided with lateral and terminal brood chambers. Its behaviour has been studied by Burmeister (1930), who shows how male and female collaborate in the excavation and provisioning of the burrow; the female does the work of excavation, while the male clears away the "spoil" through a special tunnel leading to the open; he then digs out dung from the middle of the heap and brings it to the female, who drags it down the burrow and packs it into the brood chambers which she has prepared.

Many of the Geotrupinæ, such as *Geotrupes* and *Minotaurus*, show similar reproductive behaviour, but also make food burrows beneath the dung. *Copris*, which, like the Geotrupinæ, is crepuscular in habit, stores a shapeless mass of dung for food in a cavity dug directly under the source of supply; the brood chamber she makes is larger and well finished; with the help of the male she provisions it with soft sheep dung, which she works first into a large ovoid mass then divides up into three or four pieces, fashioning each into an ovoid somewhat resembling the pear of *Scarabæus* and like it supplied with an egg-chamber and an egg. Unlike the female *Scarabæus*, she stays by her ovoids until the young beetles emerge, a matter of four months, keeping the ovoids clear of mould and herself repairing any cracks that appear. The female *Copris* is a good fashioner of dung, but neither she nor the male makes and rolls away balls of dung as does *Scarabæus*. They are probably incapable of fashioning and trundling a ball, for they lack the long curved callipers formed by the mid and hind legs of *Scarabæus*. The only ball-rollers among the dung-beetles are the Scarabæinæ, Gymnopleurinæ, Sisyphinæ and the Canthoninæ. They are all diurnal in their activity and they all possess the long curved legs necessary for ball-making and ball-rolling.

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CHEMICAL REACTIONS INVOLVING FREE RADICALS

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Though progress in all sciences is international, yet inevitably particular methods of scientific teaching immediately stimulate each new development of scientific knowledge, and consequently impose national characteristics upon scientific progress. Thus, whilst organic chemistry has, from the times of Scheele and Liebig, developed in many countries as a specialised laboratory art concerned with the study of naturally occurring plant and animal products, it has always been taught by English-speaking nations as a subject which should not be differentiated by early specialisation from cognate physical sciences. Consequently it may be noted that both in this country and in America there have been made significant applications of contemporary physical concepts in explaining the fundamental mechanisms of organic reactions. Theories of this character, which demonstrate the essential unity of the whole science of chemistry, have resulted both in the improvement of known laboratory processes and in the development of new reactions of considerable general value.

First and foremost of these theoretical contributions to the elucidation of the mechanisms of organic reactions is undoubtedly the realization by Lapworth in Manchester, over forty years ago, of the fact that many relatively slow chemical changes in solution involve the transient ionisation of certain of the reacting molecules, and the momentary liberation of highly active, charged particles, including free cations and anions derived from hydrocarbon radicals. According to this view, the activation of many organic molecules involves the *Heterolysis* of covalent bonds; bond-rupture taking place without fission of the spin-neutralised electron pair which constitutes any normal covalency, thus

$$A:B \longrightarrow A^+ + (:B)^- \quad \text{Heterolysis}$$

The qualitative application of this heterolytic mechanism for organic reactions led, a quarter of a century ago, to rational interpretations of hydrolysis, esterification, aromatic substitution, and

the principal condensation processes involved in syntheses which utilise carbonyl compounds, esters, amines and other molecules containing strongly polar groups. Valuable new syntheses, typical of which may be instanced Sir R. Robinson's adaptation of the Mannich reaction for homocyclic ring closure, have been developed by recognising that specific reactions can be induced by promoting the momentary ionisation of organic compounds of known structure. Again by developing quantitative aspects of this theory it has been possible to predict the rates of many chemical reactions in solution, to explain the nature of acid-base catalysis, and, as described in a recent article in this periodical,[1] to throw valuable light upon the stereochemical aspects of substitution processes.

Nevertheless, the heterolytic interpretation of organic reactions in solution has been shown to have its limitations, for it is now abundantly clear that there can occur in the liquid phase many chemical reactions which have all the characteristic features of gas phase reactions.

Reactions which occur in gases are much more complicated, both kinetically and analytically, than the majority of reactions in solvents such as water. They do not involve the ionisation of the reacting particles, but proceed through the *Homolysis* of covalent bonds, *i.e.* by the fission of the electron-pair bond with generation of a pair of electrically neutral, paramagnetic, radicals, or atoms, thus

$$A:B \longrightarrow A\cdot + \cdot B \quad \text{Homolysis}$$

It was again Lapworth who first pointed out that the homolysis of an isolated molecule should, in theory, require less activation energy than its heterolysis, since in the latter case work has to be done to dissociate the electrically charged particles, and he therefore stressed the significance of the solvent in bringing about chemical reactions in solution. Ionising solvents such as water, alcohol, acetic acid, etc., both by polarising undissociated molecules, and by solvating ions, reduce the activation energy for heterolytic bond fission below that required for homolytic bond fission, and these are, in fact, the types of solvents which are invariably used in the organic reactions which have already been mentioned. Conversely therefore one would anticipate that reactions occurring in non-ionising solvents, such as hydrocarbons, would probably be of the homolytic type.

The first experimental evidence for the possible existence of free neutral organic radicals in solution was actually obtained as early

[1] Cf. E. D. Hughes, "The Walden Inversion," SCIENCE PROGRESS, **34**, 516, July, 1946.

as 1900 by Gomberg, who showed that the complex hydrocarbon hexaphenylethane tended to undergo reversible thermal dissociation into a pair of chemically reactive triphenylmethyl radicals.

$$(C_6H_5)_3C—C(C_6H_5)_3 \rightleftarrows 2(C_6H_5)_3C\cdot$$

In the ensuing twenty years many analogous dissociable molecules were prepared, including derivatives of nitrogen, and oxygen, but all these molecules contained aromatic ring systems so disposed that the free radicals were in reality complex resonance systems very considerably stabilised by the dispersal of the unpaired electron between many possible localities within the whole particle. The actual existence, even in gases, of free atoms such as hydrogen was not firmly established until 1922, and not until 1929 was it shown that simple organic radicals, such as methyl, could have a real, independent existence. Even then it was felt that simple free atoms or radicals recombined so very rapidly upon all surfaces that their presence in condensed systems was virtually impossible. During the last twelve years, however, it has been shown quite clearly that free neutral radicals, of all degrees of chemical reactivity, can be liberated by homolytic reactions in solution to take part in chemical reactions which are identical in type with gas-phase processes.

Significantly enough the first experimental evidence for this theory was obtained in Manchester where, in 1934, D. H. Hey pointed out that certain of the decomposition reactions of aromatic diazo compounds in aromatic solvents led to the formation of products which did not accord with the current polarity theories. He consequently suggested that *uncharged* organic radicals might have participated in his reactions.

Hey and his colleagues showed that when several thermally unstable molecules, such as benzene-diazo hydroxide, benzene-diazoacetate or dibenzoyl peroxide decomposed in aromatic liquids, then arylation of the solvent occurred in all possible orientation positions. In particular the *para* compound $R—C_6H_4—C_6H_5$ could be isolated with ease from any solvent C_6H_5R, quite irrespective of the fact that the substituent group, R, might normally be *meta* directive, *e.g.* NO_2 or COOEt, or *ortho-para* directive, *e.g.* Cl or CH_3. This alone was strongly indicative of a reaction involving the *neutral* phenyl radical, $C_6H_5\cdot$, containing one unpaired electron, but in addition the whole reaction mechanism was substantiated by kinetic studies which showed that the rate-determining process was a unimolecular dissociation of the thermally unstable starting-product, which evidently formed highly reactive particles

capable of reacting rapidly with surrounding solvent molecules of all types, *e.g.*

$$C_6H_5—N{=}N—O—COCH_3 \rightarrow C_6H_5\cdot + N_2 + \cdot OCOCH_3 \quad \text{slow}$$
$$C_6H_5\cdot + C_6H_5—R \rightarrow C_6H_5—C_6H_4—R + \cdot H \quad \text{fast}$$

To verify Hey's theory of the transient existence of free neutral phenyl radicals in solution, the writer of this article then attempted, with success, to detect the presence of free uncharged radicals in these reaction mixtures by means of their combination with metals, such as mercury and antimony, to yield organo-metallic compounds, following, for analogy, the work of Paneth who had in this way demonstrated the formation of free methyl radicals in gaseous systems. Several decomposition reactions of aromatic diazo compounds in non-aqueous solvents were found to be capable of yielding organo-metallic compounds, *e.g.*

$$C_6H_5—N_2—OAc + Hg \rightarrow N_2 + C_6H_5—Hg—OAc$$
$$C_6H_5N_2Cl + Sb \rightarrow (C_6H_5)_3SbCl_2$$

whilst concurrently there occurred reactions involving the solvent which had been taken. For instance, when benzene diazonium chloride is allowed to decompose under acetone there occurs the reaction

$$C_6H_5—N_2—Cl + CH_3—CO—CH_3 \rightarrow C_6H_5—H + N_2 + CH_3—CO—CH_2Cl$$

in which the chlorination of the solvent is evidently brought about by atomic chlorine, for most metals, including even gold, yield their chlorides if added to this reacting system.

Reaction with solvent molecules is, in fact, typical of free neutral radicals and involves only the outermost atoms of the solvent molecules.

Once the possible existence of free neutral radicals in solution had been adequately supported by experimental evidence, such as that mentioned above, a review of those chemical reactions which were not easily explicable by the heterolytic polar reactivity theory showed that homolytic reaction processes in solution were by no means uncommon.[1] They resulted usually from reactions which involved either the thermal or the photo-chemical dissociation of an unstable molecule, and occurred most evidently in solvents such as paraffin hydrocarbons, benzene, or carbon tetrachloride, in which, of course, ionisation does not occur. Moreover, many catalysed reactions seemed to be homolytic in type, and to explain these it was again necessary to have recourse to current physico-chemical theories of gas-phase reactions.

Already the interpretation in this way of the mechanism of

[1] Hey and Waters, *Chemical Reviews*, 1937, **21**, 169–208.

catalysed reactions has had far-reaching results, which have included the discovery in both England and America of quite a number of entirely novel chemical reactions, some of which are already of technical value. In a general survey, these reactions are best considered from the aspect of fundamental theory.

According to electronic theories of valency, free neutral radicals, such as methyl or phenyl, like free neutral atoms, such as chlorine, should all, most easily, gain stability by acquiring control over one more electron, and they should therefore react:

(i) with substances which have unpaired electrons, or incomplete valency shells, *e.g.*

$$2CH_3\cdot + \cdot\ddot{\underset{\cdot\cdot}{Te}}\cdot \rightarrow CH_3:\ddot{\underset{\cdot\cdot}{Te}}:CH_3$$

(ii) with the hydrogen atoms which form the outer sheath of nearly all organic molecules, *e.g.*

$$C_6H_5\cdot + H{-}R \rightarrow C_6H_5{-}H + R\cdot$$

and (iii) with unsaturated compounds, in this case to add on to one end of the double link, *e.g.*

$$C_6H_5\cdot + RCH{=}CH_2 \rightarrow R\dot{C}H{-}CH_2{-}C_6H_5$$

Some examples of reaction (i) have already been given, but in this category must also be included recombination reactions of free radicals, *e.g.*

$$Ph_3C\cdot + \cdot CPh_3 \rightarrow Ph_3C{-}CPh_3$$

and also their very rapid reactions with "odd molecules," such as nitric oxide, which contain unpaired electrons, *e.g.*

$$Ph_3C\cdot + \cdot NO \rightarrow Ph_3C{-}NO$$

Processes of type (i) lead to the removal of free neutral radicals from reacting systems, and in the study of gas reactions the action of nitric oxide as a radical remover was shown, in 1936, by Staveley and Hinshelwood at Oxford, to be particularly valuable in the elucidation of the chain lengths of decomposition processes. Since then extensive applications of this principle in petroleum chemistry have been made in both Canada and America.

Processes (ii) and (iii), in contrast to (i), do not end chemical reactions, but are typical of the chain-propagation reactions well known in gaseous systems. The displacement reaction (ii) is typical of the behaviour of all active free neutral radicals in solution. The initial radical (*e.g.* $C_6H_5\cdot$) by picking up hydrogen (or chlorine from a chlorinated solvent) becomes a stable molecule, whilst in its place there is set free a new free radical, $\cdot R$, derived from the solvent. With these secondary radicals a series of similar displacement reactions continues until two such radicals meet and neutralise each

other, either by dimerisation (process i) or, more frequently, by *disproportionation*, one dehydrogenating the other; thus

$$\cdot C_nH_{2n+1} + \cdot C_mH_{2m+1} \longrightarrow C_nH_{2n+2} + C_mH_{2m}$$

On account of the occurrence of processes of type (ii), the final reaction product from homolytic reactions in solution is nearly always a complex mixture. Two general features of these reactions are to be noted however. Firstly, radicals typical of the solvent will be regenerated in type, but not in identity, by recurring processes such as

$$Cl\cdot + CCl_4 \rightleftarrows Cl_2 + \cdot CCl_3$$

or

$$HO\cdot + H\text{—}OH \longrightarrow HO\text{—}H + \cdot OH$$

so that, in spite of their intense reactivity, they may persist for a sufficiently long time within the liquid to react extensively with other dissolved substances. Secondly, displacement processes,

$$A\cdot + B\text{—}C \longrightarrow A\text{—}B + \cdot C$$

will be exothermic, and therefore favoured, if the resultant radical, $\cdot C$, has a lower energy content than the initial radical, $\cdot A$. In this way there may, by a suitable choice of "inhibitor" molecules, B—C, easily be produced in a system undergoing homolytic changes radicals, $\cdot C$, which are too inert to attack solvent molecules, but which remain until finally destroyed by dimerisation. Atomic iodine, and many resonance-stabilised aromatic substances obtainable by the dehydrogenation of polyphenols, or of arylamines are of this character.

Anti-catalysis of chemical change is usually explicable in this way. Its importance in the preservation of foodstuffs, fats, and oils, from deterioration by spontaneous oxidation has long been recognised technologically, but only with the advent of the free radical theory has it been possible to select the "inhibitor" or "anti-oxidant" by a rational consideration of molecular structure. The inhibition of enzyme processes, and the "poisoning" of industrial catalysts may be other actions of a similar type.

Process (iii), the addition of free radicals to unsaturated systems, can also continue as a self-propagating reaction. Thus following (iii) there can occur the sequences

$$Ph\text{—}CH_2\text{—}\dot{C}HR + CH_2{=}CHR \longrightarrow Ph\text{—}CH_2\text{—}CHR\text{—}CH_2\text{—}\dot{C}HR \longrightarrow$$
$$Ph\text{—}CH_2\text{—}CHR\text{—}(CH_2\text{—}CHR)_n\text{—}CH_2\text{—}\dot{C}HR$$

giving a saturated long chain radical which will continue to grow until again two such radicals meet and recombine, or else disproportionate. In general, the lower the concentration of the active growing chains the longer will be the chain length of the final

product. The productions of linear polymers, such as polystyrene, polyvinyl acetate, and polymethylmethacrylate (" perspex ") from monolefines and of synthetic rubbers from mixtures of mono- and di-olefines are due to chemical processes of this type. For some purposes the liquid unsaturated monomers are polymerised by dissolving in them a small percentage of a radical-producing catalyst, such as dibenzoyl peroxide, which spontaneously generates free phenyl radicals by thermal decomposition.

$$\mathrm{Ph{-}CO{-}O{-}O{-}CO{-}Ph} \rightleftarrows \mathrm{2Ph{-}CO{-}O\cdot} \quad \text{reversible}$$
$$\mathrm{Ph{-}CO{-}O\cdot} \longrightarrow \mathrm{Ph\cdot} + CO_2 \quad \text{irreversible, slow}$$

These initiate the chain addition and become incorporated into the structure of the final polymer, as has been shown by using halogenated peroxides, or aromatic diazo-compounds, and detecting the halogen in the resultant polymerised product.

For other purposes emulsion polymerisation is used. Droplets of the monomeric olefine are dispersed in an aqueous liquid containing a radical-producing catalyst, and the active free radicals then enter the dispersed drops in very low concentration, giving in this way products of very high molecular weight. Peroxides, or per-salts, *e.g.* $K_2S_2O_8$, have regularly been chosen as catalysts, and it has been found that mild reducing agents are usefully added as " promotors." Recent work at Leeds has shown that these promotors act by producing free hydroxyl radicals by a one-electron transfer in which the peroxide bond is broken by the gain of one electron from the reducing agent thus

$$Fe^{++} + \mathrm{HO{-}OH} \longrightarrow Fe^{+++} + (\mathrm{HO:})^- + \mathrm{\cdot OH}$$

Oxygen, which can add on to free radicals, in very much the same manner as can nitric oxide, is often an inhibitor of chain polymerisation, for the resulting peroxide radical may not be able to continue the chain addition process. Oxygen gas, however, can oxidise many organic and inorganic compounds by a homolytic chain reaction in which again free hydrocarbon radicals are concerned. This action, termed " autoxidation," is usually autocatalytic, but it can be initiated immediately by means of radical-producing reagents, such as the organic peroxides, or even the hydroperoxides which are formed by the autoxidation itself. In autoxidations of organic compounds the main reaction chain is a displacement process, of type (ii) involving the dehydrogenation of the oxidised material,

$$\mathrm{X\cdot} + \mathrm{R''CH_2} \longrightarrow \mathrm{X{-}H} + \mathrm{R''CH\cdot} \quad \text{chain starting by catalyst X}\cdot$$
$$\left.\begin{array}{r} \mathrm{R''CH\cdot} + O_2 \longrightarrow \mathrm{R''CH{-}O{-}O\cdot} \\ \mathrm{R''CH{-}O{-}O\cdot} + \mathrm{R''CH_2} \longrightarrow \mathrm{R''CH{-}O{-}O{-}H} + \mathrm{R''CH\cdot} \end{array}\right\} \text{chain sequence}$$

but subsequently the hydroperoxides thus formed break down, in quite a complicated manner, to yield the final oxidation products.

It is a striking feature of those autoxidation reactions which proceed at moderate temperatures that dehydrogenation of C—H groups occurs, as above, in preference to attack on double bonds. Consequently unsaturated compounds containing the —CH_2—CH=CH— group are first oxidised at the —CH_2— group adjacent to the double bond (*i.e.* in the "allyl position") and yield unsaturated hydroperoxides of the structure

$$\begin{array}{l}—\text{CH}—\text{CH}=\text{CH}—\\ \quad |\\ \quad \text{O}—\text{OH}\end{array}$$

though as these initial products subsequently break down they then appear to yield secondary radicals, such as ·OH, which do eventually attack the olefinic links. The reasons for this initial autoxidation in the allyl position can be derived quite simply by considering the stability of the possible free radicals which might be formed by dehydrogenation of an olefine, for the two structures

$$\text{A}—\dot{\text{C}}\text{H}—\text{CH}=\text{CH}—\text{B} \text{ and } \text{A}—\text{CH}=\text{CH}—\dot{\text{C}}\text{H}—\text{B}$$

represent no more than the alternative canonical states of the same resonance-stabilised free radical. Consequently the formation of this radical by a homolytic dehydrogenation process requires less activation energy than does either the dehydrogenation of a paraffin or the direct addition of a radical to one end of the CH=CH group. Compounds containing the group —CH=CH—CH_2—CH=CH— will obviously require still less activation energy for dehydrogenation, for in the resulting radical all five carbon atoms then participate in the resonance system, and it is significant that the "drying oils" used in the paint, varnish, and linoleum industries all contain this characteristic group. Resonance-stabilisation of a radical must again be considered in the autoxidation of aldehydes.

It is quite probable that free radical processes also play an important rôle in biological oxidations, for many enzyme-catalysed oxidations, when examined *in vitro*, have been shown to have the kinetic features of chain reactions. Again, a few of the essential prosthetic groups of oxidation-reduction enzymes, as for instance the vitamin riboflavine, have already been shown to be capable of yielding free neutral radicals by partial reduction, whilst some biological products, such as hæmatin, can be used as autoxidation catalysts. Free hydroperoxides are not found in living cells, however, since they are rapidly destroyed by the ever-present enzyme "catalase," which probably acts upon hydrogen peroxide in very much the same manner as does any ionised ferrous salt.

As yet, however, the cogency of the free radical theory in this borderline between chemistry and physiology has scarcely been explored. Its investigation will be no easy task, since it is difficult to pick out a diagnostic free radical process in even a simple organic reaction.

Though chain polymerisation and autoxidation are by far the most outstanding of the technically important reactions in which free neutral radicals are concerned they are by no means the only chemical reactions to which the modern homolytic theory has brought a valuable insight. Many, though by no means all, addition reactions of olefines have turned out to be homolytic processes of type (iii) and not heterolytic processes.

For instance, when hydrogen bromide is mixed with an unsymmetrical olefine, addition normally occurs as follows

$$R—CH{=}CH_2 + H—Br \longrightarrow R—CH(Br)—CH_3$$

in accordance with Markownikow's empirical rule which states that "the hydrogen atom tends to attach itself to a CH_2 group in preference to a CH group," and which can be deduced, quite simply, from the well-known polar theories of chemical reactions involving ions (*e.g.* the ions H^+ and Br^-). In 1933, however, Kharasch and Mayo, in Chicago, found that in the presence of quite a small percentage of a peroxide a much faster abnormal reaction occurred in the reverse direction, thus

$$R—CH{=}CH_2 + H—Br \xrightarrow[\text{catalyst}]{\text{peroxide}} R—CH_2—CH_2—Br$$

The discovery of this "peroxide effect" accounted for many of the anomalies reported by earlier workers, and led to the discovery of quite a number of new addition reactions of distinct synthetic value. For example, in the presence of peroxides, bisulphites and thiols can both be made to add on to olefines: in the absence of peroxides such additions do not normally occur.

The "peroxide catalysed" addition of hydrogen bromide to an olefine has the following chain mechanism:

(*a*) The peroxide slowly generates a trace of an active free radical, *e.g.*

$$Ph—COO—OCOPh \rightleftharpoons 2Ph—CO—O\cdot$$

(*b*) The active radical abstracts hydrogen from hydrogen bromide (so also from a bisulphite or a thiol), *e.g.*

$$Ph—CO—O\cdot + H—Br \longrightarrow Ph—CO—O—H + \cdot\ddot{\underset{\cdot\cdot}{Br}}:$$

(*c*) The bromine *atom* then adds on to one end of the double bond. Being a neutral atom, with an incomplete shell of but seven

electrons, it tends to acquire stability by completing its octet. To effect this it must gain some control over one more electron, and this it can do, with the least energy requirement, if it attacks the C=C bond at the point of highest electron density. This is usually the site of the CH_2 group, not the CH group, for in molecules such as $CH_3—CH=CH_2$ or $Cl—CH=CH_2$ the substituent (CH_3 or Cl) tends to drive electrons away from it during chemical change, or, in other words, tends to stabilise the radical $CH_3—\dot{C}H—CH_2Br$ or $Cl—\dot{C}H—CH_2Br$ either by electrostatic action or by a resonance effect.

Consequently homolytic addition takes place as follows

$$R—CH=CH_2 + \cdot\ddot{\underset{..}{Br}}: \rightarrow R—\underset{\cdot}{C}H—CH_2—Br$$

(*d*) Process (*c*) above leaves a free carbon radical, which, like the initial catalyst, can dehydrogenate hydrogen bromide

$$R—\underset{\cdot}{C}H—CH_2Br + H—Br \rightarrow R—CH_2—CH_2—Br + \cdot\ddot{\underset{..}{Br}}:$$

and so the process can go on, via reactions (*c*) and (*d*) in turn, until one of the reagents is used up, or one of the participating radicals is destroyed by a side reaction.

Typical of these side reactions will be reactions between the organic radical $R—\underset{\cdot}{C}H—CH_2Br$ and substances, such as quinol or diphenylamine, which can lose hydrogen homolytically even more easily than can hydrogen bromide. Compounds such as those named above may therefore be used to "inhibit" peroxide-catalysed addition: they do not affect the "normal" (*i.e.* ionic) addition.

Hydrogen bromide is the only one of the halogen acids with which this abnormal, peroxide-catalysed, addition reaction can be carried out. Hydrogen fluoride and hydrogen chloride are both too stable for dehydrogenation by peroxide radicals, whilst hydrogen iodide would yield atomic iodine which is not sufficiently reactive to attack a C=C bond, and merely dimerises to molecular iodine. Actually, iodides are inhibitors of nearly all homolytic reactions.

The addition of bromine to olefines can also take either the heterolytic or the homolytic course according to circumstances. The latter mechanism is favoured by non-ionising solvents, such as benzene or carbon tetrachloride. Light promotes this type of reaction by dissociating a trace of the molecular bromine, and so producing the active bromine atoms with which the chain reaction can be initiated. Atomic bromine, however, can dehydrogenate reactive C—H groups, such as the active $—CH_2—$ in $—CH_2—CH=CH—$

or the side chain in toluene. Indeed, substitution of aromatic compounds, such as toluene, in the side chain is characteristically a homolytic process, whereas substitution in the aromatic nucleus is usually a heterolytic process. Thus the conversion of toluene to benzyl chloride is favoured by heat and light, conditions which favour dissociation of molecular chlorine to atomic chlorine, and set up the chain reaction :

$$Cl_2 \xrightarrow{\text{light}} 2\ \cdot\ddot{\underset{..}{Cl}}:$$

$$\left.\begin{aligned} :\ddot{\underset{..}{Cl}}\cdot + CH_3{-}C_6H_5 &\longrightarrow H{-}Cl + \cdot CH_2{-}C_6H_5 \\ Cl_2 + \cdot CH_2{-}C_6H_5 &\longrightarrow Cl{-}CH_2{-}C_6H_5 + \cdot\ddot{\underset{..}{Cl}}: \end{aligned}\right\}\text{chain}$$

In 1939, Kharasch and his colleagues showed that sulphuryl chloride, SO_2Cl_2, was a very convenient reagent to choose for carrying out homolytic chlorinations of this type. Benzyl chloride can be obtained in high yield by dropping sulphuryl chloride slowly into boiling toluene containing a trace of dibenzoyl peroxide as a catalyst. The reaction depends in part upon the ease with which sulphuryl chloride can dissociate to sulphur dioxide and chlorine, since the rapidly attained equilibrium

$$SO_2Cl_2 \rightleftarrows SO_2 + Cl_2$$

will be shifted to the right by the chlorination process which ensues. The unstable radical $\cdot SO_2Cl$ may also be concerned, however, since in the presence of pyridine or quinoline toluene can be sulphonated in the side chain, giving $C_6H_5{-}CH_2{-}SO_2Cl$.

Certain organic chlorinating and brominating agents, as for example N-chloro-imides, such as $(Cl_3C_6H_2){-}N(Cl){-}CO{-}C_6H_5$, and N-bromo-imides, such as N-bromo-succinimide, can be used in the same way. Since they attack the $-CH_2-$ group and not the double bond in the system $-CH_2{-}CH{=}CH-$ they are proving to be very valuable reagents for conducting specific degradation reactions of complex natural products. It is significant too that these same reagents are autoxidation catalysts.

More and more of these specific homolytic reagents are being discovered as time goes on. One of the most interesting of these is lead tetra-acetate, which is often used, in glacial acetic acid solution, as an oxidising agent. At moderate temperatures it dissociates reversibly to free acetate radicals

$$Pb(O{-}CO{-}CH_3)_4 \rightleftarrows Pb(O{-}CO{-}CH_3)_2 + 2\ \cdot O{-}CO{-}CH_3$$

and can be used for the oxidation of glycols, which it splits to aldehydes or ketones. In hot acetic acid solution, however, acetate radicals, like benzoate radicals (from dibenzoyl peroxide), break

down irreversibly giving carbon dioxide and the very much more active free radical methyl, which can dehydrogenate almost any C—H group.

$$CH_3—CO—O\cdot \rightarrow \cdot CH_3 + CO_2$$

Consequently hot solutions of lead tetra-acetate oxidise toluene in the side chain, benzyl acetate being the final reaction product. Even acetic acid is attacked by the methyl radicals, for in 1943 Kharasch and Gladstone showed that both methyl acetate and succinic acid could be obtained by decomposing diacetyl peroxide in hot glacial acetic acid.

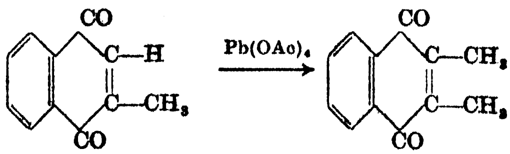
This surprising reaction probably proceeds as follows:

$$CH_3—CO—O—O—CO—CH_3 \rightleftarrows 2CH_3—CO—O\cdot \rightarrow \cdot CH_3 + CO_2$$
$$CH_3—CO—OH + \cdot CH_3 \rightarrow \cdot CH_2—CO—O—H + CH_4$$
$$2\ \cdot CH_2—CO—OH \rightarrow HO—CO—CH_2—CH_2—CO—OH$$

and

$$CH_3—CO—O\cdot + \cdot CH_3 \rightarrow CH_3—CO—O—CH_3$$

A year earlier Fieser and his colleagues at Harvard University had discovered another new reaction of lead tetra-acetate, which again indicated that free methyl radicals were produced during its decomposition in hot acetic acid. In attempting to oxidise a quinonoid compound with lead tetra-acetate they found that their product had been methylated, and thereupon were able to show that the methylation of quinones was quite a general reaction. Thus



Under similar circumstances, dinitrobenzene gave dinitro-toluene, whilst benzene gave a small amount of benzyl acetate. All these processes undoubtedly involve reaction between free methyl radicals and the C=C bonds of quinonoid or aromatic systems.

Many further instances of the recent discovery of new homolytic reactions could be cited,[1] but there is not the space to enumerate them all in this general article. It should already be clear to the reader, however, that all these free radical processes proceed in a manner that is now clearly predictable by reference to the three general reaction types given on page 27. As yet, however, too little experimental work has been carried out for it to be safe for any theoretical chemist to declare whether or not any particular

[1] For a fuller account of this "New Organic Chemistry" the reader may refer to the writer's monograph *The Chemistry of Free Radicals* (Oxford, 1946).

free radical will have a sufficiently high energy content to attack any one specific C—H group, or double bond, in a given complex organic molecule. In the study of homolytic gas reactions a great deal has been done towards accumulating this important information,[1] but even in this field chain reaction processes are often proving to be too complex for analysis with certainty. In chemical changes involving free radicals in solution even more alternative reactions have usually to be considered, so that as yet it is rather premature for the physical chemist to take over the quantitative development of this new branch of organic chemistry. Nevertheless, the notable developments of this subject in both England and America during the past ten years would not have been possible if the experimentalists in both countries had not been clearly aware of the value of approaching their subject by considering carefully its fundamental basis—the molecular and atomic mechanism of all chemical change.

[1] *Cf.*, for example, *Atomic and Free Radical Reactions*, by E. W. R. Steacie (Reinhold Pub. Corp., New York, 1946).

SCIENTIFIC LOCUST CONTROL

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THE locust problem has confronted man ever since he attempted agriculture. There is a picture of a locust on the wall of an Egyptian tomb of the Twelfth Dynasty, about 2500 B.C., and locusts were one of the Twelve Plagues of Egypt. References to this pest and the damage it caused abound in Hebrew, Greek, and Chinese texts, and Roman writers have left many data. The modern literature on the subject is enormous and contributions have been published in a dozen languages testifying to the seriousness of the problem and its wide range.

The area of the world affected by the locust and its smaller relative, the grasshopper, is not often realised by the general public. The ravages caused by these pests in Africa and the Middle East are much in the public news, but it is not generally realised that the problem is also a very real one in Soviet Middle Asia where the Asiatic Migratory locust periodically causes immense damage to the cotton fields and other crops. In China the Oriental Migratory locust has repeatedly caused wholesale famines and its range extends to the Philippines, Indo-China, Malaya, and the Indonesian islands. Australia also has its locust and grasshopper problems. Both the United States and Canada have to wage an incessant war against grasshoppers, and wide areas in South and Central America are periodically devastated by the American locust.

In Africa and the Middle East, the region with which we in this country are more immediately concerned, there are three species of locust of great economic importance and it is with these that our anti-locust control is more directly concerned.

The first of these is the Desert Locust (*Schistocerca gregaria*). It is this species that has been known to man since biblical times and it is still as active as ever. The area it covers is enormous, stretching from India in the east to the Atlantic coast of Africa in the west, and in the north from Russian Turkestan to the British Colonies and Protectorates south of the Equator in East Africa. The second species is the African Migratory Locust (*Locusta migratoria migratorioides*), which has its centre in the bend of the middle

Niger and which periodically swarms over vast areas of the African continent.

The third species is the Red Locust (*Nomadacris temfasciata*), which is chiefly found to the south of the Equator and periodically ravishes Rhodesia and neighbouring Belgian and Portuguese territories and extends into the Union of South Africa.

It is difficult to assess the damage and actual loss caused by locusts, although it is a fact that great famines have been caused by locusts in India, China, and other places. In Tanganyika Territory 75 per cent. or more of the native crops were destroyed in 1929 and great damage was also done in Kenya. In the countries of the Middle East facts are often difficult to collect, as these areas are sparsely inhabited and communications are inadequate. Nevertheless, the Anti-Locust Research Centre attempted to reach a figure for the ten-year period 1925–35. Statistics could only be obtained from 49 countries out of the 77 suffering from the pest, and yet the figure arrived at was staggering, as it showed that crops to the value of over 80 million sterling were devoured by locusts in that period, and this in spite of the defensive measures taken, which undoubtedly saved many crops, but cost 13 million pounds.

For hundreds of years man has been striving against the locust, but it has been defensive warfare. The locust usually exists in a solitary state in areas remote from settled cultivation and is then more or less harmless. Under certain conditions, however, it may start laying eggs and rapidly increases in numbers until the swarming stage has been reached. The life cycle is fairly simple. The eggs are deposited in packets, containing 30 to 100 eggs, in the soil. In temperate regions they lie dormant in the winter, but in the tropics they may hatch out in two or three weeks if there is sufficient moisture. The hoppers emerge from the eggs and grow rapidly, moulting four or five times before the adult stage is reached. The whole cycle occupies a year in temperate regions, but in the tropics there may be several generations in the year, and that is one of the reasons why the locust plagues are worst in the warmer parts of the world. One of the chief differences between the grasshoppers and locusts is that the hoppers of the grasshopper group live independently, whereas locust hoppers congregate in dense masses or swarms and so cause the crop damage that is so much feared. Urged by impulses which are not at present fully understood, these swarms, consisting of millions of individuals, start moving out of the desert into the more settled areas and as they move leave a trail of devastation behind them. These invasions

do not come at regular intervals and there is no definite cycle, and consequently the result, in the past, has invariably been that man was not ready when the attacks commenced. The age-old measures of poison baiting, trapping in trenches and so on, have to be got under way, involving the assembly of materials, transport, and labour in large quantities, with the result that by the time operations are effective much of the damage to crops has already occurred.

After an invasion there has been a natural and understandable reaction, with a tendency on the part of the Government concerned to lie back with a sigh of relief and trust that a similar invasion will not recur for many years. The result has been that no prolonged or planned offensive has ever been waged against the locust and no progress has been made towards the final elimination of the menace until recent years. Recently, however, it has come to be realised that the aim should be the permanent control of the locust by scientific measures. The credit for this new outlook on the locust problem must go to a large extent to the British Government, who have led the way in the new policy.

When a serious outbreak of the desert locust started to develop in 1928, the British Government decided that, not only should defensive methods be continued, but that a radical solution of the problem should be sought by investigating the reasons for the periodical swarming of locusts, with a view to their control. A Locust Sub-Committee of the Committee of Civil Research (later transformed into the Committee on Locust Control of the Economic Advisory Council) was formed in 1929 and the actual work was entrusted to a special research unit under Sir Guy Marshall, then the Director of the Imperial Institute of Entomology. The technical direction was in the hands of Dr. B. P. Uvarov, whose subsequent researches have proved of such great value and who still continues in charge of the Anti-Locust Research at the present time. The first step was to devise a scheme for collecting current information on locust movements and breeding, particularly in Africa and the Middle East, as it was felt that it would be wise to concentrate largely on these regions. Investigators were sent out to study the conditions on the spot, and the organisation speedily attracted the attention of other countries interested in the problem.

At the first of several International Locust Conferences held at Rome in 1930, the British organisation was requested to act as the International Centre for Anti-Locust Research and the following eight years witnessed a unique concentration of scientific effort. Parties of British, French, Belgian, South African, Indian, and

Egyptian entomologists systematically explored one area after another. Representatives met nearly every year to pool results and plan for the future. The information so gathered was accumulated at the Locust Centre in London and a unified reporting system was evolved, covering Africa and a substantial part of Asia. The results of this team work have been amply justified. At the outset very little was known about the distribution of the different species of locusts in Africa, or of their seasonal cycle and migrations, or about the origin and course of the periodical outbreaks. But after eight years a clear picture of the factors became available and it was possible to outline a definite policy aiming at a radical solution of the whole locust problem.

It was abundantly evident that the periodicity of locust incursions was closely connected with the transformation of the harmless solitary phase into the dangerous gregarious one. It was also proved that this transformation can only happen in certain restricted areas, having peculiar natural conditions, and that only in these outbreak areas can the first swarms be started.

The outbreak area of the red locust has been located in Northern Rhodesia and adjoining parts of Tanganyika, and to keep a watch on this area an Anti-Locust Unit has been formed, with headquarters at Abercorn. Similarly, the outbreak area for the Migratory Locust is in the middle bend of the Niger in the French Sudan, and here a unit is maintained by the French.

With regard to the desert locust, it was found that swarms can arise from certain scattered areas along the Red Sea littoral in Arabia, Somalia, in Baluchistan and Mauretania. The headquarters for these areas is at Cairo. Each of these three units kept in close touch with the Anti-Locust Centre in London and relied on it for technical supervision and advice.

By the time of the declaration of war in 1939, the Anti-Locust Centre in London had become the main headquarters for direction and advice for all locust control efforts in these areas, and it was in constant touch with other scientific bodies in America and elsewhere who were faced with similiar locust and grasshopper problems. At first annual surveys on the locust position were provided to all Governments affected by the locust problem, but for the last three or four years the reports and information received are so abundant and exact that monthly bulletins are issued. These bulletins contain a summary of the situation for the previous month, give a brief forecast of the developments to be expected during the next month, and are accompanied by a small-scale map showing the general situation. More recently still it has been found

possible to send brief forecasts by air, and special warnings of sudden new developments may be sent out, with the object of giving the Governments of the countries concerned as much time as possible to complete their preparations if a campaign should prove necessary against invading swarms.

An essential part of the work is the accumulation and dissemination of data. Annual bibliographies of current literature have been published and abstracts of papers supplied to officers in the field. Extensive collections of locusts and insects associated with them have been made and their parasites studied, and the basis of a library has been collected. Much of the research undertaken in those pre-war years was directed towards obtaining information with regard to the effect of geographical and climatic conditions on the habits of the locust. By means of the system of reporting described above, it was found possible to reconstruct the normal annual cycle of the three kinds of African locust and to forecast with some certainty the breeding periods and migration routes. Similarly, bio-climatic research has lead to useful results, and in regard to one area of the Desert Locust, *viz.* East Africa and Somaliland, some suggestive correlations of seasonal locust activity with climatic data have been found.

The headquarters of the Anti-Locust control centre are at the British Museum (Natural History). The accommodation available is limited and the opportunities for laboratory work are very restricted. Research actually at the centre has necessarily, therefore, been largely confined to bio-geographical and bio-climatic research, deducted from the reports sent in, and much of the other valuable research that has been accomplished has been undertaken by officers attached to the centre who have proceeded to the locust areas for field research with specific problems in view. Thus one problem was to study locusts in the solitary phase and to try to elucidate the biological and climatic factors which may influence them to concentrate and eventually to transform into the gregarious phase. This was followed by studies of the factors regulating the behaviour of gregarious hoppers and adults of the Desert Locust.

One interesting piece of research indicated that the solitary phase is capable of migrations at least as extensive as swarms in the gregarious phase.

The advent of war in 1939 coincided with signs of renewed swarming of the Desert Locust after a quiet interval of several years. Owing to war conditions it was not possible to observe the first swarms and to send out the usual warnings, nor was it possible to organise a campaign for their destruction. By the time the

Middle East became more accessible, however, swarms were sufficiently widespread to necessitate an urgent campaign for the protection of crops in the Middle East and in East Africa. In a way, war conditions proved a blessing in disguise for locust research, because the vital importance of safeguarding the food supplies, so necessary for troops and population alike, ensured the willing co-operation of all the Governments concerned. This made possible for the first time a unified campaign embracing the whole of the affected area, and operations assumed an offensive character rather than a defensive one, as had invariably been their nature in the past. The organisation of the locust campaign was taken over by the Middle East Supply Centre, who recruited a special staff of entomologists and locust officers for field operation to supplement those provided by the Governments concerned, namely, Kenya, India, the Anglo-Egyptian Sudan, and Egypt. For the first time, it was possible to study the problem in some of the key countries of Arabia, which were formerly inaccessible for all practical purposes, and much information of the greatest value for the future has been gleaned.

The control of locusts in the field entails much material and labour, which has to be transported often under conditions of great difficulty, for the early locust swarms are usually to be found in some of the most inhospitable and undeveloped regions in the world. The transport of the necessary labour, of their food and water and the supplies of bait and other material is a big problem, but the co-operation of the Military and Air Forces which was readily forthcoming rendered the campaign feasible. This is not the place to recount the results of this locust campaign, but to record the fact that, as it took place during the war, it permitted actions to be taken which would not have been possible under peace conditions and gave the scientists who took part in the work an unrivalled opportunity of observing new features and of getting new ideas which should do much to render locust control an easier task in the future. At the commencement of the campaign the time-honoured method of control, namely, the use of poisoned bait, had perforce to be used. This method, which consists of placing mounds of bran or fodder poisoned with sodium arsenite in the path of the advancing swarm, involves a tremendous amount of transport and labour and is not only extremely costly but presents difficult administrative problems. In addition, the use of sodium arsenite is objectionable, as it is poisonous to livestock and care has therefore to be taken to keep village cattle and other livestock away from the environment. A search for another

form of bait was, therefore, initiated and eventually it was discovered that the synthetic substance "666" (hexa-chloro-cyclohexane), later named gammexane, served the purpose admirably. It is harmless to cattle, but is deadly to the locust. Its effect is not instantaneous, but the insect that once comes in contact with it invariably dies. Nevertheless, it would appear to be desirable to endeavour to find an insecticide with all the good qualities of gammexane but having a quicker lethal action, as this would have a better psychological effect on the native farmer and help to convince him of the efficacy of the remedy. In view of the cost of employing paid labour, the long-term policy must naturally be to encourage the farmers themselves to employ remedial measures to save their own crops and, in order to gain their confidence, they must be convinced that the remedies proposed are really efficacious. When a locust is affected by gammexane it may go off apparently unharmed and it may prove difficult to convince the farmer that it will eventually succumb. It would be advantageous, therefore, if an insecticide with a quicker "knock-out" effect could be devised. The danger of using a material poisonous to stock has been obviated to a large extent, but there still remains the high cost of transporting large quantities of bait in the form of bran, hay, or grass to the spot. Experiments to get over this difficulty have now been initiated.

The difficulties and cost of the method of ground baiting naturally led those engaged in these operations to consider whether it would not be possible to effect control from the air by means of suitable dusts or sprays. Considerable progress has been made in recent years in the control of certain insect pests by means of sprays or dusts distributed by aircraft, as, for example, the control of the Boll weevil in the cotton fields of America, and by some of the work undertaken in Soviet Russia, but these methods have only been applied to a previously known and stationary target, such as a field crop or a forest which is being damaged by a pest. With locusts the problem is more complicated, as the insecticide has to be applied to a swarm which only remains for a short time in a given area. Further, the actual location of the swarm may only become known immediately beforehand and it may be outside the range of the nearest airfield or landing ground. The time during which dusting is possible depends mainly on the factors which cause the locust to rest on the ground or on vegetation or to take wing again. These factors are not yet clearly understood and indicate the need for more research, but, as the urgency for trying out new methods of attack was at the time extreme, it was

decided to make immediate trials rather than to postpone the effort indefinitely until fuller information was available. Accordingly with the willing co-operation of Middle East Air Command a small Anti-Locust Flight was organised and equipped with dusting apparatus.

The first trials were intended to be carried out in Baluchistan, but as, for some unpredictable reason, the locusts failed to materialise in that region, the Flight was transferred to Kenya, where opportunities for field tests were found.

The practical results of these tests with dusts were rather disappointing. The poison used, D.N.O.C. (di-nitro-ortho-cresol) dust, proved to vary in its toxicity, apparently due to variations in the air humidity. Further, the lethal dose per acre was found to be so high that it was impossible to cover the swarm within the time, with the type of aircraft available. Nevertheless, the experience gained was extremely valuable, as the complex nature of the problem became evident. A clearer idea of the kind of poison required and the type of aircraft and distributing apparatus necessary was obtained, and this has led to the formulation of a definite programme of research to solve these problems. Incidentally it was found that D.N.O.C. when used as a dust from the ground proved effective against hoppers. However, one of the disadvantages of the dusting method as compared with baiting is that the machinery needs skilled labour and technical supervision, which is costly and not always readily obtainable.

In 1945 the opportunity was taken, while service aircraft and personnel were still available in the Middle East, to carry out trials with sprays instead of dust. These trials were under the circumstances rather makeshift, as much improvisation had to be undertaken. Different methods of spraying from the air were tested, namely, "air-to-ground" spraying against settled locusts, "aerial-curtain" spraying against fully flying swarms, and "static curtain" spraying against rolling swarms. Preliminary experiments on another species of locust made at the Porton Research Station in Wiltshire, to whose willing co-operation in research matters the Anti-Locust Centre is greatly indebted, had indicated that a certain strength of D.N.O.C. in a mixture of gas and lubricating oil might prove effective. It was realised at the start that information about the toxicity of D.N.O.C. to flying locusts was not really adequate, that not enough was known about the behaviour of flying swarms in the field and other important matters, and that the tests were bound to be of a preliminary nature. Conditions for these trials were not entirely favourable, because all

the swarms met were "rolling", *i.e.* partly flying and partly settled. Nevertheless, certain general conclusions were reached. It is considered that air-to-ground spraying against settled locusts is capable of development into a control method as soon as suitable aircraft, such as helicopters, can be used for swarm reconnaissance and delimitation. Also that aerial-curtain spraying against fully flying swarms is a promising method and should be the subject of further research immediately. It promises the economical protection of one region from invasion from another. It is considered, however, that static-curtain spraying against rolling swarms has only a limited application, but should not be abandoned unless other modes of attack in this kind of swarm can be evolved.

The main result of these extensive measures against the desert locust, during the war period, was that an opportunity was afforded for trying out theories and new methods of control, but it soon became obvious that before some of these ideas could be really applied on a large scale much more definite information would have to be obtained and that the answers could only be supplied as the result of research, much of this being of a fundamental nature.

Accordingly it was decided to widen the scope of the Anti-Locust Centre in London. Since 1929 it has functioned as a small section of the Imperial Institute of Entomology, but in 1945 it was established as an independent research institution, financed by grants from the several British Overseas territories that are affected by the locust plague and from the Colonial Research and Development Fund. The staff has been increased to meet its enlarged functions; Dr. B. P. Uvarov continues to be the Director, with Dr. D. L. Gunn as Principal Scientific Officer. The latter officer had gained much experience whilst supervising the field experiments and trials in the Middle East, which have been mentioned above. The research activities of the centre are directed by a Scientific Committee consisting of specialists in entomology, insect physiology, ecology, meteorology, toxicology, and aircraft methods of insect control. All are members either of a University or a scientific institution which is likely to be interested in one of the many problems awaiting solution.

The investigations carried out by the Anti-Locust Centre during the pre-war years have, as has already been mentioned, led to much enlightenment on the problems that obscured locust control. The large-scale field experiments that were rendered possible during the latter part of the war period widened our knowledge in many respects and pointed the way to several new and promising lines

of attack. At the same time it is realised that there are many gaps in our knowledge which will have to be bridged before really practicable and efficient measures can be recommended for routine application for dealing with future locust outbreaks. Many of these problems involve fundamental research and will need to be carried out in the research laboratories in this country, where facilities exist for carrying out the necessary studies. It would be utterly impracticable to attempt to conduct such investigations under desert conditions. Nevertheless, it is realised that the research worker in England must make himself familiar with conditions in the field and it is highly desirable therefore that, where possible, visits should be arranged, so that he may be able to acquaint himself with the habits of the locust under natural conditions.

It is not proposed to organise further extensive research at the Anti-Locust Centre itself. As has been mentioned, accommodation is strictly limited, and the provision of the extra laboratories would hardly be justified, since it would mean duplicating special equipment which is already available at other research institutions in this country. The Centre has already undertaken certain lines of investigation and will therefore continue its biographical and climatic researches. It will also continue to breed locusts to meet the requirements of other research workers in this country. Locusts have been bred at the Centre in the British Museum (Natural History) for years past, but the technique of producing locusts of the desired phase in numbers is still insufficiently known. For example, research is needed to find out the best diet for locusts in captivity. There are several investigations of a fundamental nature which need to be organised extra-murally. Some of these are already being handled adequately, others it is hoped will be investigated with the assistance of members of the scientific committee. It will be worth while, at this point, to consider some of these fundamental problems which it is hoped will be examined in the research laboratories in this country. There is, for instance, the problem of contact poisons. As has been mentioned in an earlier part of this note, considerable progress has been made with the introduction of gammexane in place of sodium arsenite, and there is always the possibility that further contact poisons of even greater potentiality may be developed. The great drawback to this baiting method is the high cost of transport involved in the conveyance of large quantities of bran or other fodder and of the labour required to handle it. As the outbreaks usually occur in sparsely inhabited districts, or even in desert regions, there is also

the problem of supplying rations and water for the staff employed. Any measure that can be devised to cut down these costs will therefore be a definite advance. This has led to the consideration of the use of rolls of cheap fabric, such as hessian, which can be impregnated with a suitable contact poison. The suggestion is that this material should be unrolled in the path of an advancing swarm. The locusts will have to cross this "magic carpet" and so will make contact with the poison and succumb to its effects. The carpet can then be rolled up and used over and over again. The project is not so fantastic as it might appear on first consideration. In fact, small-scale tests in this country have already shown that gammexane may prove a suitable poison for this purpose and that any locust that crosses over the "carpet" will succumb. Steps are therefore being taken to test out the scheme under field conditions in Africa as soon as possible and the results will be awaited with interest.

Problems connected with the physiology and the mechanics of locust flight need study. The preliminary trials with spraying from the air have shown that more knowledge is required about the factors affecting the structure and density of swarms, their ground and air speed and so on. Our present knowledge of the mechanics of locust flight is meagre and exact studies in a laboratory equipped with a wind tunnel may prove necessary. Such studies may help us to understand the physiology of the flying locust and shed light on the reasons for long-distance migrations.

Work is also required on the physiology of vision. Recent work tends to attribute importance to visual reactions, not only during mass movements, but also in the process of swarm formation and the maintenance of cohesion, but our existing knowledge is extremely limited.

Again there is the question of phase physiology. It is believed that the basis of locust swarming is to be sought in physiological changes associated with the visible phase variation in colour and structure, but no serious work on the general metabolism of the different phases or on the significance of pigmentation has yet been undertaken. Such work can only be carried out in special laboratories by physiologists and biochemists.

Another problem refers to migration cycles in their relation to climatic considerations, and several other lines of work which need to be investigated could also be mentioned, but enough has been said to indicate the scope for fundamental work of this nature in this country. With the assistance of members of the Scientific Committee, it is hoped to secure the co-operation of certain specially

equipped laboratories by offering research grants, and so secure the services of well-qualified research workers who would undertake some of these lines of research.

In conclusion, an endeavour has been made in these notes to show how the war on the locust has in recent years at last moved from the defensive, in which condition it has remained throughout the ages, to the offensive. The action taken by the Anti-Locust Centre, backed by the British Government, to achieve this position has been indicated and the effect of war conditions in stimulating activity described. Great progress has been made in the last twenty years, but big problems remain to be solved. The need for fundamental research in this country and of applied research in the regions affected by locusts is abundantly evident, and the need for the closest co-operation of all workers on these problems is obvious. The enthusiasm and energy excited by war conditions must not be allowed to die away.

COSMIC RAY MESONS

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1. In one of the classical experiments of cosmic ray physics, Bothe and Kohlhorster showed that, contrary to expectation, the very penetrating part of the cosmic ray beam consisted of charged particles. These, the "hard" particles, as they came to be called, were readily identifiable in cloud chamber photographs when these were taken, and such photographs gave much more detailed information about them, for in the cloud chamber the particle momentum may be measured from track curvature in a uniform magnetic field, and the ionisation density along the track determined as a function of momentum. Although all the penetrating particles were likely to be of a kind, particular significance attached to those particles of cosmic rays photographed in the cloud chamber which were clearly of the penetrating group and which lay in the particular momentum range $2 \cdot 10^8$ ev./c. – $7 \cdot 10^8$ ev./c.* Below the lower limit, particles unambiguously belonging to the penetrating group were not identified in the earlier measurements, but within this range the density of ionisation of the particles was such that it was possible to say with certainty that they were not protons, for the upper limit of momentum quoted is that below which proton tracks in the cloud chamber become conspicuously heavily ionised, while the corresponding tracks of penetrating cosmic rays were of the thinly ionised condition characteristic of all singly charged particles at extremely high energy.

If these particles were not protons, it was equally certain that their behaviour was not that to be expected of electrons. At high energies, the loss of energy by electrons should be predominantly in radiative collisions; the rate of loss should be proportional to energy and of such a magnitude that electrons would be essentially non-penetrating. Two interpretations were possible of the penetrating nature of the hard cosmic ray particles: either the large

* The electron volt divided by the velocity of light is a convenient unit of momentum for problems involving very energetic particles, since under extreme relativistic conditions momenta in these units and energies measured in electron volts are numerically equal.

loss of energy in radiative collisions predicted by theory is suppressed at high energies, or the particles are not electrons but are, rather, heavier particles for which radiative loss of energy would not become important in the practical range. Of these alternatives, the former was first postulated, partly because the temper of the time was against the ready acceptance of completely new types of fundamental particle, partly because the separation at a momentum limit of about $2 \cdot 10^8$ ev./c. of soft particles (normal electrons) below, hard particles above, is remarkably complete, and partly because this particular limit is, to order of magnitude, that at which the classical self-reaction forces of a radiating electron become of compelling importance. It was supposed [1] that at this momentum a cut-off of radiative collisions takes place and that at still higher momenta the radiation emitted by a fast electron traversing matter is negligible. Three lines of evidence served to make the position outlined untenable:

(i) Anderson [2] showed that the real distinction between hard and soft particles lay, not in a critical momentum limit, but rather in whether or not the particles in question were shower particles; particles causing showers, or members of showers of associated particles, were of one kind, probably electrons, and it was the particles which seemed not to be members of showers, but which appeared always alone in cloud chamber photographs, which were penetrating.

(ii) Blackett and Wilson [3] showed that, whatever might be the reason for the absence of radiation by the penetrating particles, the scattering of these particles, which also takes place in the Coulomb field of the atomic nuclei of the matter traversed, showed no anomaly, and

(iii) Williams [4] showed that it was necessary, if most artificial assumptions were to be avoided, that normal scattering should be accompanied by normal radiation.

The credit for positive evidence of the alternative hypothesis, that the penetrating particles are heavier than electrons, belongs to Anderson, who obtained a photograph in which a penetrating particle reaches the condition of heavy ionisation in a cloud chamber working in a magnetic field. The mass of this particle was deduced to be about $200m_0$ (m_0—the electron mass), and the type of particle came to be known as "mesotron" or "meson." *

* Of various names put forward, "meson" and "mesotron" have been extensively used. The latter was proposed by Anderson, but it was pointed out by Bhabha that consistency of derivation required the form "meson," and this has come to be generally accepted.

2. Up to the present time, our only source of mesons is in cosmic rays, and it is useful to summarise the nature and quantity of the supply from this source.

The sea level flux of mesons is about 100 per second across a horizontal square metre. Of these about 8 have momentum less than 5×10^8 ev./c., 16 between 5×10^8 ev./c. and 10^9 ev./c., and about 12 greater than 10^{10} ev./c. The remainder are in the momentum range $10^9 - 10^{10}$ ev./c.; the maximum of the momentum spectrum lies at about 7×10^8 ev./c. [5].

The total meson flux increases rapidly with altitude and the increase is almost entirely concentrated in the low momentum region. Comparable spectrum figures at high altitudes are not available.

The characteristic property of mesons in cosmic rays is their penetrating power. Direct measurements [6] have shown that mesons traversing matter suffer no additional loss of energy at all comparable with that due to ionisation of the material traversed, which may be regarded as an inevitable minimum for a charged particle. Thus mesons are as penetrating as is possible for charged particles.

3. The discovery of a particle in nature with a mass about 200 times that of an electron directed attention to a theoretical prediction by a Japanese, Yukawa, made in 1935, in which the existence of such particles was postulated. Yukawa developed a theory of the short-range force between the heavy particles in atomic nuclei in close analogy to the electromagnetic field. The static Coulomb interaction of electromagnetic theory with the potential $\phi = q/r$ was replaced by a short-range interaction of the form $\phi = g\frac{e^{-\lambda r}}{r}$ (where g is a charge-like constant, and the range of the force is of the order $1/\lambda$); then, as the electromagnetic wave equation may be considered as giving the probability distribution of free photons, so the corresponding Yukawa wave equation describes the free motion of certain particles. Unlike photons, these have a finite rest mass, $\mu = \frac{\hbar}{c}\lambda$, ($\hbar$ = Planck's constant/2π), and since, experimentally, the range $1/\lambda$ of the nuclear forces is of the order of the classical electron radius,

$$\mu \sim \frac{\hbar}{c}\frac{m_0 c^2}{e^2} \sim \frac{\hbar c}{e^2} m_0 \sim 137 m_0$$

The Yukawa theory, with affinities on the one hand to electromagnetic theory, is closely related on the other to the Fermi-Heisenburg development of β-decay and nuclear forces (see, for

example, 5, below). In particular, the electron-neutrino exchange of the Fermi theory has its analogue in a Yukawa particle exchange. The phenomenon of β-decay thus requires, in addition, that the Yukawa particle shall itself be unstable, decaying with the prototype of β radioactivity into an electron and a neutrino. The mean lifetime of this particle was estimated by Yukawa to be about 0·5 microsecond.

When the possibility is recognised that the cosmic ray meson may in fact be the particle predicted by Yukawa (we will in future refer to this as the "Yukawa meson" or as the "nuclear force meson"), it becomes essential to know, firstly, whether cosmic ray mesons are unstable; secondly, if so, what are the products of disintegration; and, thirdly, what is the lifetime of such a meson. Firm answers to all of these three questions are now available.

That mesons do decay was first demonstrated as follows: the intensity of penetrating particles at a high-altitude station is measured, and also the reduction in intensity by a certain additional lead screen (some lead screening will be already in use to discriminate between the penetrating and soft components). Knowing that, so long as it exists, the loss of energy by a meson is almost exclusively by ionisation, we may calculate the thickness of air below the station of observation which is equivalent in ionisation effect to the additional lead screen. A third measurement of intensity, without the additional screen, is made at this depth in the atmosphere below the high station. A comparison is now available of meson loss in a thin lead plate and in an equivalent air layer; if the loss in air is greater, the interpretation is that this is so because the air and lead layers are of differing thickness, because the large air layer offers opportunity for mesons to decay while the small thickness of lead does not. This result was in fact obtained, and the meson lifetime was found to be of the order one microsecond. The amount of decay which actually occurs in the air layer of such an experiment is small, for, while the distance travelled at the velocity of light (to which all mesons concerned approximate) in one microsecond is only 1,000 feet, the relativistic transformation of time measurements between the frame of reference at rest relative to the meson and the practical frame of our observations is by a factor $p/\mu c$, where p is the momentum of the meson and μ its mass, a factor which for the majority of mesons is large.

This direct demonstration was preceded by the observation that several obscurities of existing experimental material might be resolved by the postulate of meson decay. These included, notably, the differences of meson absorption coefficient in vertical and

inclined directions measured at heights in the atmosphere at which the equivalent mass thickness of the air layer traversed in the various directions was the same, and the observation that the cosmic ray intensity at sea level shows a strong negative correlation with atmospheric temperature. In the latter case, for example, we assume that mesons, being unstable, are of terrestrial origin ; since mesons are not observed to be produced in appreciable quantity at sea level, the production must, in the main, take place in the upper layers of the atmosphere. When the air is warm, the distance from these layers to sea level is greater than it is when the air is cold ; accordingly, the opportunity for mesons created high in the air to decay before they reach sea level is greater when the atmosphere is warm, and the total number arriving at sea level is smaller.

The direct experiment outlined above is not suitable as the basis of an accurate determination of the meson decay time. Quite apart from other uncertainties, the accuracy of such an experiment is essentially limited by that of our knowledge of μ, which, we shall find, is not of high precision. Accurate determinations of the meson decay by Rossi and his co-workers [7] in America and by Freon [8] in France have been of a different kind. Traversing matter, a meson has a certain possibility of decay and has also an actual, continuing reduction of energy ; it is to be determined from the relevant constants whether, on the average, a meson is likely to decay while its energy is still considerable, or whether, on the other hand, the probability is large that the meson will be stopped completely by the ordinary processes of energy loss before it has an appreciable chance to decay. It is found that, while in air a meson is likely to decay before it has been slowed down to rest, in solid absorbers the chance of decay before the particle has been slowed down to rest is negligible. Rossi and Freon, therefore, observe the time that elapses between a meson entering into and stopping in a block of metal, and the product of decay, an electron, leaving the block. They thus measure the decay of mesons at rest, and the result can be interpreted without the mediation of a Lorentz transformation of doubtful magnitude. The results of the two groups of observers agree excellently :

Rossi and others	$\tau_0 = 2{\cdot}15 \pm 0{\cdot}07$	microsecond
Freon	$\tau_0 = 2{\cdot}2 \pm 0{\cdot}2$	microsecond.

The whole method of these measurements implies that the decay of mesons involves the emission of a fast ionising particle. The check of this fact is of the kind which is as a rule obtained by cloud

chamber methods, but in this particular case the situation is complicated, in so far as the conditions suitable for precise measurement are not the same as those leading to a high probability of detecting a decay event. A certain number of cloud chamber photographs exist in which the heavy track of a slow meson is seen to end in the midst of the chamber, and in which from the endpoint of this track the thin straight track of the decay particle is seen, making a random angle with the end of the meson track. There is little doubt that the thin track is that of an electron, but the precise measurements of energy which are needed to complete the identification with the type of decay predicted by Yukawa have not yet been made. However, there are some examples in which it seems clear that no decay electron has been emitted. There are indications that it is the negative mesons that behave in this way, and the discrepancy is interpreted as follows. Decay of the free meson at rest takes place only for positive mesons; free slow negative mesons have a capture probability by atomic nuclei that is high compared with the decay probability, and are therefore always captured before they decay. If this view is accepted, it leads to considerations about the absorption of a meson by a nucleus which may be of the greatest theoretical importance. The situation is still not understood, but there are obvious difficulties in explaining the entry of an energy of 10^8 ev. without complete disruption of the recipient nucleus.

5. The experiments described, and particularly those of Rossi, lead to a fairly accurate value of the lifetime of cosmic ray mesons. Since the qualitative correspondence between the cosmic ray meson and the Yukawa meson is complete, it becomes important to determine whether this value can be incorporated into the theory in place of Yukawa's rather smaller value.

Re-examination of the Yukawa treatment which has been carried out by Nordheim [9] and others leads to the conclusion that the cosmic ray lifetime value is not consistent with that demanded by nuclear constants; indeed, it appears that the Yukawa value, far from being low, is a large overestimate. This conclusion is based mainly on the value used by Yukawa for the G function of the Fermi theory of β-decay. This quantity is determined from direct observations of β-decay, and is found to vary considerably according to the group of radioactive elements that is considered, although its value within a group may be reasonably constant. In particular, the light artificial radioactive elements lead to a value very much larger than do the heavy natural radioactive bodies. Yukawa uses the value for heavy elements, but it is precisely for this group that the constants of decay must depend to some extent

upon quantities other than G. It seems certain that the value deduced from light elements is to be preferred in estimating the meson lifetime. Making this adjustment, and others of less importance, Nordheim gives a lifetime of less than 10^{-8} second, a value differing by a large factor from that of the cosmic ray meson.

If the cosmic ray meson and the nuclear force meson cannot be regarded as one and the same single particle, the similarity between them is striking. This similarity is at present explained by the assumption that more than one kind of free meson may exist, and, while a meson with the revised Yukawa properties makes the chief contribution to β-decay, the actual mesonic field involves components leading in the free state to cosmic ray mesons also, and, it may be, to other varieties. We refer later (8) to the Møller-Rosenfeld theory of the nuclear field. These workers show that, for a certain form of interaction, the observed properties of the simplest nuclear structures demand a mixed field involving both vector and pseudoscalar functions. The field will be described in this way both in respect of the interaction between nucleons and also during the process of formation of free mesons ; however, as soon as the mesons formed may be regarded as free, no significant interaction between the field components will remain, and there will be, for purposes of observation, a mixture of mesons of two or three kinds. It is still necessary, in this picture, that mesons of very short lifetime should result at meson formation, and up to now these have not been identified. Even if the lifetime of these so-called "short life mesons" is as large as 10^{-8} second (and there are grounds for supposing that it is very much less), the difficulties of detecting and identifying them are great, and the failure to do so is not to be regarded as an indication that such mesons do not exist.

6. The classical observation of Anderson established that some mesons in cosmic rays have a mass of about $200m_0$. The question whether there is a unique mass, whether in fact all mesons are of mass about $200m_0$, has in the last few years produced a variety of answers, partly because the theoretical position is sufficiently fluid to put no restraint on such speculations, and partly because the technique by which mass determinations in the mesonic range are made is capable of large errors which are almost immune from any process of check. These peculiarities of meson mass measurements are so important that some comment upon them is necessary ; we will first, however, state the conclusions which may reasonably be drawn from the existing evidence.

Knowledge of the mass of cosmic ray mesons is based on the study of the cloud chamber tracks of much less than fifty individual

particles. These photographs establish that the great majority of cosmic ray mesons are of about $180m_0$, with a probable error of between $10m_0$ and $20m_0$ (the critical error study on which this figure is based is not complete enough to make a closer estimate of the probable accuracy possible). There is also evidence, not yet certain but compelling serious attention, that a relatively small group of particles are of mass about $1000m_0$. At the time of writing, there is no comparable evidence of "light mesons," although such particles have from time to time been reported. The following table lists individual measurements for which the several authors claim accuracy of about 15 per cent. or better, and probably includes the majority of reliable values.

MASS MEASUREMENTS OF INDIVIDUAL MESONS

Method.	Observer.	Mass in Terms of m_0.
Elastic collision with electron	Leprince Ringuet	240 ± 20
	,, ,,	990 ± 100
	Hughes	180 ± 25
Momentum loss traversing plate	Nishina	180 ± 20
	Wilson	170 ± 20
Momentum and ionisation	Williams & Pickup	160 ± 30
	Nielsen & Powell	210 ± 20
	,, ,,	180 ± 20
	,, ,,	190 ± 15
	,, ,,	145 ± 30

The determinations are based on three types of observation:

(i) conservation relations for elastic collisions of mesons with electrons in which the energy transfer from meson to electron is almost the maximum possible. Used in particular by Leprince Ringuet and his co-workers [10].

(ii) simultaneous measurements of momentum and track ionisation. For example, Williams and Pickup [11].

(iii) measurements based on the range-momentum relation for a charged particle near the end of its range;

(iii) (*a*) mesons stopping in the gas of the cloud chamber,

(iii) (*b*) using change of momentum for the traversal of a metal plate by a slow particle. Nishina [12], Wilson [6].

All of these are possible only for mesons for which v/c is appreciably less than unity, that is, for mesons in a small range of energy, which, moreover, are passing out of that range rapidly because of the increase of ionisation with decreasing velocity. Measurements are, therefore, possible only for a small fraction of mesons.

Although other factors are involved, that which effects all

methods critically is the measurement of momentum. The precision of this quantity is governed by uncertainties of two distinct types: first, the uncertainty of the actual path pursued by the particle, arising from the scattering of the particle in the electric fields of atomic nuclei; secondly, the shortcomings of technique which introduce errors between the actual description of a particle trajectory and its eventual measurement as a cloud chamber track photograph. The second factor, which is not assessible without intimate knowledge of the history and routine of a particular apparatus, is the chief obstacle to the correct weighting of various determinations; broadly, however, it becomes less serious as the magnetic field in which momentum is measured increases. The first, which has been the subject of an important study by Williams [13], is much more serious than was at one time realised, and sets a fundamental limit to the performance of any particular arrangement of apparatus. It also becomes less important with increasing magnetic field, but at any particular value of field sets a limit to attainable accuracy. This limit may be reduced by using a gas in the cloud chamber which scatters less (*i.e.* one composed of atoms of low Atomic Number), but this remedy is unfavourable to methods (i) and (iii) (*a*), which depend on the amount of scattering or on closely associated properties for the frequency of occurrence of the event sought, a frequency which is always tediously low. For the accuracy which has already been reached, it excludes the use of high-pressure chambers in all fields, method (iii) (*a*) in all fields and all other methods in low fields (up to 1000 gauss). Method (i) reaches maximum accuracy at a certain intermediate value of field (3000–4000 gauss), but the other methods gain continuously with increasing field. The methods likely to lead to more accurate determinations than are now available are (ii) and (iii) (*b*); method (i) is in most factors comparable, but here increased accuracy is purchased only by coming to a quite unacceptably slow rate of occurrence.

Measurements at all comparable with those by which the electron and proton masses are known are not yet in sight. It is most unlikely that the existing technique in which two measurements, often with conflicting requirements, are made in a single cloud chamber is capable of an order of magnitude improvement, and it is probable that the next advance will make use of systems of cloud chambers, each adjusted to the optimum conditions for a single variable. The first actual step in this direction was reported at the Physical Society Conference in Cambridge (July 1946) by Leprince Ringuet.

The evidence for the possible heavy meson rests on early observations by Williams and Pickup [11] and Anderson [14], setting

rather wide limits, and on observations of two kinds by Leprince Ringuet [15], one of which appears in the table of accurate values.

The decay of fast mesons while traversing a layer of the atmosphere is essentially a measure of the quantity τ_0/μ, and Rossi and his co-workers [16] have carried out experiments in which attention is confined to particular groups of mesons covering in each case a definite small range of momentum. They give the result,

$$\frac{\tau_0}{\mu} = (8{\cdot}3 + 0{\cdot}6).10^{-4} \text{ cm. c/ev.}$$

which, combined with the accurate rest determination of τ_0, leads to

$$\mu \doteqdot 155m_0.$$

If this result could be assumed free from disturbing factors, it would rank as the most accurate value of μ; it would be of particular interest, moreover, because it is an average value taken over all the penetrating particles in a given momentum group. However, the possibility cannot be excluded that a limited amount of meson formation takes place within the layer of atmosphere considered. It is better to take this result together with the accepted mass determinations as an indication that meson formation in these layers, if occurring at all, is on a very small scale.

7. The preceding paragraphs emphasise the difficulties which attend measurement of even the simplest and most direct properties of cosmic ray mesons. These difficulties are enhanced when the finer properties of mesons engage attention, and the results at present available are meagre and uncertain. It is probably correct to regard the provision of data in this field as the most pressing requirement of experimental fundamental physics to-day.

Important properties to which attention has been directed are:

(i) spin;

(ii) interaction with nucleons without capture (nuclear scattering);

(iii) production; the main process in the atmosphere, probably nucleon-nucleon collisions;

(iv) production; in large electron-photon cascades, probably photon-nucleon collisions;

(v) capture of slow negative mesons by nuclei.

We will discuss only (iii) and (iv) in any detail; of the other headings, (v) has already been referred to, the spin (i), which is certainly from general considerations either 0 or 1, has been studied by Lapp and others, with results which can scarcely yet be regarded

as conclusive, and the scattering (ii) has been measured by Wilson [17], Code [18] and Shutt [19] to order of magnitude, although the important energy variation has not yet been established.

We have already quoted strong grounds for supposing that almost all meson production takes place high in the atmosphere. It is possible to use the temperature coefficient of meson intensity and the directional anomaly of atmospheric absorption to arrive at an effective level of meson formation ; for most purposes this may be taken to be at a depth of one-tenth of the atmosphere from the top.

Very extensive work has been done by Schien and his co-workers to investigate the region of meson formation by means of counter systems carried by free-sounding balloons, but the interpretation of this work suffers seriously because of the high intensity of soft cosmic rays which is present, the effect of which it is difficult to determine. Balloons will not carry the thick layers of lead screening which would effectively exclude the disturbing influences.

It is on account of these screening difficulties in balloon work that the best study of meson formation yet available is that carried out by Janossy and his colleagues in Manchester during the last few years, at sea level where the rate of meson formation seems to be only of the order 1 in 10^5 existing mesons. The drawbacks of a very slow rate of production have been more than met by the freedom of geometry, by continuous counting for months on end and by the availability of any reasonable amount of lead screening. This work was initiated to study so-called "penetrating showers"—associated particles capable of producing effects at penetrations in lead very much beyond the range of electron cascades ; it therefore strictly detects meson formation only under conditions where two particles at least are suitably associated, but Janossy has pointed out that, particularly in heavy elements, this must be expected to be the rule, for the cross-section of a nucleon-nucleon collision is such that, if a collision takes place with one nucleon, others will almost certainly take place with other nucleons in the same nucleus, and so a group of several mesons will be formed by collisions at a single nucleus.

The results of this group of experiments can be summarised as follows. Penetrating particles, almost certainly normal mesons, are formed by isolated entrant particles, probably protons and neutrons. Only one meson-producing particle is found at sea level for about 10^5 mesons, and the precise number exhibits an extremely strong barometric effect, the effect, we think, of alterations of the thickness by weight of matter through which the particles entering

the atmosphere must pass to reach us at sea level. The thickness reducing the number of particles to a fraction $1/e$ appears to be 100 gm./cm^2 in air, and this implies that, of incident cosmic ray primaries reaching the atmosphere from outside the earth, only a fraction e^{-10} can reach sea level. The production of associated groups of penetrating particles by this incoming component shows a transition curve in lead placed above the apparatus which approximately saturates in from 5 to 10 cm. of lead. The transition efficiencies of lead and paraffin in similar geometries have been compared, and the efficiency is found to be mass-proportional. Superposed upon this effect is a second of great importance, which has been separated from the first in an investigation by Janossy and Broadbent [20] (this reference also covers, directly or indirectly, the greater part of other work by this group of workers). Penetrating showers, that is, closely associated groups of at least two meson-like particles are found also to be associated with the dense parts of extensive air cascades. Broadbent has shown that these are certainly secondary to the electron-photon complex of the shower, and gives evidence that they are particularly located in the core region. He further shows that here the density of mesons in the shower has a mean value as high as about one in fifty particles. The implications of this work are not yet fully worked out. It is clear that the second effect covers a distinct mode of meson production, involving light particles (electrons or photons), and it may well be that the mesons formed in this way are not identical with normal mesons. This speculation, and the problem of the disposal of the rather large numbers of mesons which appear to be produced, are subjects for early clarification.

The theoretical treatment of the problems of meson production has been given by Hamilton, Heitler and Peng, and by Heitler and Walsh [21]. Although yielding valuable results, the treatment also serves to emphasise the limitations of the existing formalism as applied to meson problems. It is necessary, for example, to treat the important nucleon-nucleon collision in the Weizsäcker-Williams semi-classical approximation, for a rigorous treatment is much more intractable than is the corresponding radiation problem. But the validity of this method is open to serious doubt ; can, for example, the transformation from proton to neutron or vice versa properly be regarded as a small perturbation ?

8. It has been the intention of this article to discuss the experimental background of the cosmic ray mesons, but frequent reference has been necessary to the meson field theories of nuclear force which have come into prominence since the existence of mesons was

established, and which provide the main reason for the importance attached at present to cosmic ray investigations.

The general picture of meson theories to-day is unsatisfactory : more is needed than the application of the existing treatments, and the time is ripe for fundamental advances. Meanwhile the situation offers a close parallel to that of atomic theory in the early 1920's. Yukawa's theory, as was that of Bohr, is clearly correct in broad terms, but the superposed pieces of machinery, now as then, are laboured efforts. The paucity of definite and precise experimental data, moreover, is a most severe handicap.

It is perhaps useful in conclusion to summarise the main guiding ideas behind the most effective detailed theoretical development, that of Møller and Rosenfeld [22]. This treatment postulates meson fields corresponding to both charged and uncharged particles combined in a way due to Kemmer, which leads to approximately equal interaction both between like nucleons (that is, proton-proton or neutron-neutron) and between unlike nucleons (neutron-proton) ; both the broad features of nuclear structure and the results of scattering experiments make this approximate equality of interaction essential. Wave functions respectively of scalar, pseudoscalar, vector and pseudovector type, leading in each case to wave equations satisfying the conditions of relativistic invariance and definite positive energy, are then developed. A static interaction between nucleons is separated by methods analogous to those leading to the Coulomb interaction in electromagnetic theory, and the significance of this separation is discussed. Finally, Møller and Rosenfeld proceed to distinguish between the four types of wave function which are formally possible, in terms of two criteria. Firstly they consider the treatment of the strong dipole interaction arising from a pure vector wave function, and give reasons for rejecting treatments of this interaction by means of cut-off conditions. They conclude, therefore, that the acceptable combination of wave functions must be chosen from the outset so that the dipole interaction is zero. Secondly, they introduce the known properties of the simplest atomic nucleus—the deuteron. Scattering experiments have shown that the static potential in the deuteron is attractive in two energy states ; the two states have been identified and the energies determined. These facts, together with the elimination of the dipole interaction, are sufficient to determine a combination of the four types of wave function. If only two are combined, these must be the vector and pseudoscalar functions, and, although a mixture of more than two types could not be distinguished on these criteria, these two functions necessarily occur, and the simplest alternative is adopted.

As is pointed out in an earlier section, the combined meson field function derived in this way will lead, in processes in which free mesons are produced, to a simple mixture of different kinds of free particle. Only one of these particles has up to now been identified with certainty and provided with experimentally determined constants. The possible existence of other mesons is thus a critical point; and there are good reasons for supposing that two most promising indications on the subject lie in the heavy mesons identified by Leprince Ringuet and in the cascade-produced mesons studied by Janossy and Broadbent.

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RECENT WORK ON FLAGELLAR MOVEMENT

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Introduction

Probably everyone is familiar with the common monoflagellate organism, such as Euglena, consisting of a single cell with a flagellum attached, and in our student days most of us were taught that by the simple lashing of this flagellum the cell was either pushed or pulled through the water.

The matter is, however, far more involved than would at first appear, and is of fundamental importance from the point of view of evolution, for, while we are fully familiar with limb-movement whereby a limb is freely moved by means of muscles controlled by nerves, in the monoflagellate we have free movement taking place within the flagellum in which there is not a vestige of a sign of either nerve or muscle.

The matter becomes still more interesting when it is remembered that the flagellate organisms were probably the first free-swimming organisms to appear in the Earth, and possibly the first living organisms which ever existed. Finally, flagella or cilia occur almost throughout the whole realm of living organisms in some form or other not excluding man himself, where they play a vitally important part in reproduction and also in most of the sense organs.

However, we are here concerned chiefly with flagellar movement, and the main point to be discussed is " How can a flagellum by its simple wagging from side to side propel the cell and where does the energy come from ? "

A great impulse was given to the investigation, in this country, by the publication in 1928 of *Ciliary Movement* by James Gray, and in the preface to this book Gray states : " Any real conception of ciliary movement must eventually rest on a proper understanding of the hydrodynamical problems which are involved. At present little is known of the forces which surround very small elongated structures which are moving through the water at very low speeds. In a few places I have tried to indicate the value of such knowledge

and in doing so I have run considerable risk of error. Should such errors attract attention and thereby lead to a better understanding of the facts, one of the main purposes of this book will have been fulfilled."

It was certainly Gray's work which stimulated my own investigations on flagellar movement, but unfortunately it would appear that many who have read parts of *Ciliary Movement* and copied its statements word for word failed to observe the caution mentioned in the preface; and finally some of the errors which have since come to light, such as the misrepresentation of Krijgsman's diagrams of the swimming of Monas, or the misstatements about the swimming of Peranema "*after Verworn*" can hardly be described as incorrect speculations.

Flagellar Movement

This will be discussed here under the following headings:

(*a*) The structure of the flagellum.

(*b*) The relationship of the flagellum to the cell.

(*c*) The nature of the origin of the energy within the flagellum.

(*d*) The mechanics involved in locomotion.

The Structure of the Flagellum

There is no need to discuss this point in the following article, since it has been dealt with so ably in the U.S.A. by Harley P. Brown who, by means of the electron microscope, has established the following facts.

(*a*) The flagella studied are of approximately uniform diameter throughout their entire length.

(*b*) Each flagellum consists of a denser axial core (axoneme) and a less dense sheath surrounding the core.

(*c*) The core, in the flagella of Euglena and Astasia, appears to consist of two closely approximate fibres of equal size.

(*d*) The sheath appears to contain or consist of a coiled fibre which encircles the axial core in a helix.

(*e*) In many flagella there are either single rows or numerous rows of delicate filaments or "Flimmer."

Excellent photographs are given of all these structures and for further details the original paper must be consulted.

The Relationship of the Flagellum to the Cell

The point at issue here is, or was, "Does the cell supply the flagellum with all its energy or does the flagellum generate its own energy?" In other words, is the flagellum an active unit, so far

as energy is concerned, or is it completely passive? Gray argued, though partly on quite false grounds, that the flagellum could not be a passive unit. However, he put forward a suggestion by which this point could be proved.

The following will, I think, illustrate the line of investigation which was carried out.

Fig. 1, Plate I, shows a piece of fine string about 6 feet long suspended from the spindle of a small electric motor.

Fig. 2, Plate I, shows the same string when the motor is in motion and the string rotating fairly rapidly.

Obviously energy is being supplied to the string from the one end only, and since the string is doing work in overcoming the resistance of the air the energy is getting less and less towards the free end of the string. This shows itself by a regular shortening of the waves.

It is true that there is a very slight increase shown in the amplitude of the waves but this need not be discussed here. Suffice it to say that both *wave-length and amplitude* could not remain unaltered unless some means were found to supplement the energy within the string itself. In other words, under the influence of impulses generated at the one end only, either the wave-length or the amplitude must decrease.

The same holds good for the flagellum, for as the waves pass along it they must be doing work in overcoming the resistance of the water, and unless the energy is reinforced the waves must get either slower and slower, or shorter and shorter, or the amplitude must get less and less.

Waves passing along the flagellum on the monoflagellate Peranema have been investigated by means of the film and it has been proved that as they pass along from base to tip of the flagellum there is a definite increase in velocity accompanied by an increase in amplitude. Hence the energy imparted to the flagellum from the cell must be supplemented by energy generated within the flagellum itself.

The Nature of the Origin of the Energy within the Flagellum

Since the flagellum is now known to consist of an axoneme, a sheath, and an outer surface covering, it would seem highly probable that energy derived from the cell is transmitted to the flagellum by the axial core and supplemented by energy generated as a surface reaction in the flagellum.

On this point there is no definite information, except that it is known that the rate at which the waves pass along the flagellum is

FIG. 1.

FIG. 2.

almost infinitely slow compared with the rate at which an impulse passes along a nerve fibre, and this is strongly suggestive that the energy in the flagellum is transmitted as a surface reaction, or in other words the energy is transmitted from molecule to molecule. It should be noted, however, that the structure of the protozoan flagellum as revealed by the electron microscope is practically identical with the structure of the sperms of the fresh-water ostracods. These sperms are highly motile under the proper conditions and, since they are relatively enormous, they can be examined and even dissected under quite low powers of the microscope. In these sperms it is definitely established that there are two types of movement, one of which is definitely due to the axial core, while the other is equally definitely due to a surface reaction. The counterpart of the protozoan cell is practically absent in the ostracod sperm, the sperms comprising something of the order of 99·9 per cent. flagellum.

In the protozoan flagellum, in the absence of definite information, it is only reasonable to suppose that the initial impulse is generated within the cell and transmitted through the axial core and the impulse is of a chemical nature. This impulse is, in its turn, supplemented by the surface reaction, but I would stress the point that, so far as the protozoan flagellum is concerned, there is no definite information beyond the very slow rate at which the waves are propagated along the flagellum.

THE MECHANICS INVOLVED IN LOCOMOTION

The problem is a difficult one and one on which there has been a great deal of controversy. For a very able discussion of this controversy Harley Brown's paper should be consulted with its very full list of references.

Gray thought that the waves or impulses could start from either

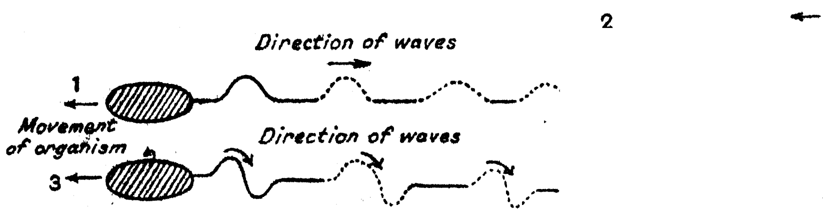

FIG. 3.—Diagram illustrating the dependence of the direction of movement of an organism on the direction of the waves which pass along its flagellum.

1. The waves originate at the base of the flagellum and travel straight along it to its tip: the animal moves straight ahead with the flagellum pointing backwards.
2. The waves originate at the tip of the flagellum and pass to its base: the animal moves with the flagellum in front.
3. The waves originate at the base of the flagellum and pass along and round it in a clockwise direction: the animal moves with the flagellum behind and at the same time rotates in an anti-clockwise direction.
4. The waves originate at the tip and pass backwards with an anti-clockwise rotation: the animal s with the flagellum in front and rotates in a clockwise direction.

end of the flagellum and the waves might be of a spiral nature in some cases, while in others the vibrations could be confined to one plane only.

The diagram (Fig. 3) on page 65 taken directly from *Ciliary Movement* (p. 34, Fig. 33) gives Gray's solution of the problem.

Unfortunately this diagram has found its way into numerous text-books, elementary or otherwise. It is true that it was put forward tentatively, but the fact remains that not one of the four figures given can be in any way applied to any known monoflagellate. The film has shown that in all flagellate organisms so far investigated the waves or impulses always start at the base of the flagellum and never at the tip. All waves are of a spiral nature.

In all simple monoflagellate or biflagellate organisms the flagella are always attached to the anterior end. Swimming is always accompanied by rotation and gyration.

Actually this rules out both the older tractellum and pulsillum theories and leaves the road clear for the newer and less-speculative concept of the rotating inclined plane or the propeller.

The final blow both to the tractellum and pulsillum theories was given when it was discovered at Plymouth that the simple organism *Monas stigmatica* Pringsheim was capable of attaining a speed of over 40, or in other words it traversed over 40 times its own length in a second. No flagellum could either push or pull an organism through the water at this speed.

There is no need to enlarge on the misconception of the tractellum theory, but since it still persists the following is added. The length of the flagellum of Euglena is practically two and a half times the length of the organism. Thus if the organism were 10 units long the flagellum would be 25. No. 4 of Gray's diagram is the only one which could possibly apply to Euglena (a so-called tractellum). But Gray gives the rate of beat of the flagellum of Euglena (which is the rate at which a wave passes along the flagellum) as 67 per *minute*, which is practically one beat per second, while he gives the relative speed of Euglena as 3–5 or, in other words, on our figures given above the organism would have a speed of from 30 to 50 units per second. Thus the organism would be travelling at a greater speed than the wave in its flagellum which is supposed to be pulling it forward. Clearly if waves did travel from tip to base along the flagellum and draw the organism forward the speed of the waves would have to be considerably greater than the speed of the cell. Gray has unfortunately given or quoted figures which make it less. Though we know very little about the forces surrounding very small elongated bodies moving through the water at low speeds,

surely we know enough to realise that Gray's figures present something which is not in accordance with ordinary mechanics.

THE PROPELLER CONCEPT

It is impossible to explain this fully here but the following experiment (Fig. 4), readily done by anyone, will, I think, make the concept clear. C is a small electric motor with a cork attached to the

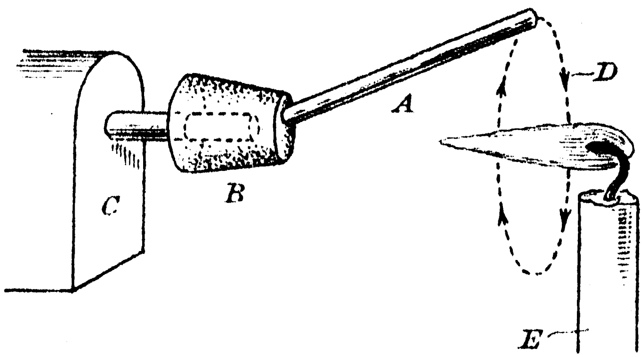

FIG. 4.

spindle. A small stick A (a part of a dissecting needle) is attached as shown. On starting the motor the stick or elongated body is made to both rotate and gyrate, with the result that air is drawn in as indicated by the flame of a candle. It makes no difference whether the motor rotates in a clockwise or anti-clockwise direction.

It is, of course, dangerous to compare a minute organism under water with a relatively large rigid stick attached to a motor, but this simple experiment was made the basis for a long series of experiments in which short flexible leather thongs were made to rotate and gyrate under water at very low speeds.

From these experiments it was definitely established that so long as an elongated body is made to rotate and gyrate under water, the necessary component force was produced by which the organism would be driven forwards.

Harley Brown carried the concept still further by carrying out an ingenious experiment in which he made a small model of *Monas stigmatica* and caused it to rotate and gyrate under water. He also carried out a series of swimming experiments under water in which he made himself his own mono-flagellate, and he has fully confirmed the concept.

So far then as the mechanics of propulsion are concerned, the matter can be summarised as follows.

1. The primary function of the flagellum, in a monoflagellate organism, is to cause the *organism* both to rotate and gyrate about a certain axis which constitutes the main direction in which the organism is swimming.

2. The mechanical principle involved is simply that of the rotating inclined plane or propeller.

3. The flagellum itself may or may not produce an additional forward component. In Euglena where it is swung back it actually does so, but in Menoidium where it is swung out at right angles it does not.

4. There is no evidence of any kind that the waves ever start at the tip of the flagellum and thus constitute a tractellum.

It is equally impossible for the flagella, in normally swimming organisms, to be attached to the hinder end of the organism and to push the organism through the water.

A full list of references is given in Harley Brown's paper so there is no need to repeat them here but, apart from the investigation with the electron microscope, the paper is chiefly concerned with further experimental proof of the *Propeller Concept*.

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"EX FUMO DARE LUCEM"

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On the strength of Faraday's dictum that man's position in the scale of civilisation is measured by his methods of illumination by night, the efforts 150 years ago of William Murdoch and Philippe Lebon to give to the world gas-lighting are worthy of commemoration. One must include the Frenchman's name as well as that of Murdoch whenever the development of illuminating-gas is mentioned. For although wood-gas with its high proportion of carbon dioxide was destined to pass into insignificance when ousted by coal-gas, to be burned under the Jumbo wood distillation retort as a subsidiary distillation product, Lebon's thermo-lamps following his faith in wood as raw material for gas-making form a chapter full of import. Moreover, wood and coal distillation, apart from being developed in the same period by two pioneers working independently, were closely connected in products other than gaseous ones. In the rise of the coal-tar colour industry methyl alcohol played a prominent part; and methyl alcohol in those days was always wood alcohol.

The struggles of Lebon and Murdoch were likewise comparable in certain respects. Both were engineers of a kind, closely interested in steam engines. Murdoch had his steam "road engine," a tricycle arrangement including a copper boiler and spirit lamp, a device which rather startled the Redruth vicar when he met it on the churchyard path by night; and his later more major products designed while with Boulton and Watt, these including an oscillating engine and the casting of jacketed cylinders in one piece. Philippe Lebon—sometimes called D'Humberson to distinguish him from his brother—had passed first through the mathematical and drawing school of Châlons-sur-Marne and then through the École des Ponts et Chaussées before becoming engineer in the corresponding Department of Bridges and Roads, and ultimately winning a national prize of 2000 francs for improvements to a steam engine. And both men, despite every drawback and discouragement to their schemes, became attracted to the idea of gas illumination in the same period, *viz.* in the 1790's. (This is to ignore early dabblings, possibly legendary at times, in destructive distillation. There is still told

the old Cumnock tale that Murdoch's first essay in gas-making was attempted in an old tea-pot ; and a second version of his seeing gas issuing from a piece of coal in the fire, of his being inspired to use a pipe as retort and igniting the gas issuing from the stem.) There is probably more truth than any fireside reverie in Lebon's first effort while visiting his father at his native Brachay, when he heated a glass vessel containing sawdust and ignited the issuing gas.

In their urge to prepare gas as an illuminant from wood and coal, Lebon and Murdoch provided the stimulus which converted a carbonisation process into one of distillation. Wood distillation had been born as a charcoal-burning process in Predynastic times ; had provided a black pigment for tomb paintings of the Nineteenth Dynasty ; and charcoal had to be made before the first smelting of metals. But no condensate was thought of, apart from tar which Pliny records as being recovered by roasting in ovens, the tar being used for preserving ships " and the bodies of dead men." But after Glauber in 1658 had shown the identity of the acid in pyroligneous liquor with that in vinegar, and Boyle had separated a " spirituous liquid " from pyroligneous acid, the time was ripe for someone to go further and give us that distillation process which gave us wood alcohol as solvent, acetates as mordants, and acetone for cordite. That person was Lebon, providing the impetus in his gas-making researches to look to volatile products. Just 150 years ago, while Lebon was at work in France, the first British charcoal factory was set up on the borders of Sherwood Forest to provide charcoal for the Sheffield industry, a factory which was to become our first and foremost wood distillation factory.

There is, then, the claim for better recognition of Lebon's work on wood-gas ; the claim that, despite the ultimate eclipse of wood-gas as illuminant in face of Murdoch's coal-gas, Lebon's work brought on that early nineteenth-century activity in winning products from forests and woodlands. Ovens and retorts with all kinds of condensing systems, designed for yielding a " spirit from the wood " more potent than the poet's, were set up once methyl alcohol and acetic acid became recognised—for coal-tar dyes and in dyeing. Coke displaced charcoal in the blast furnace, coal-tar creosote outbid wood creosote as preservative, coal-gas completely banished wood-gas ; but still wood distillation was kept alive by demands set up in developing coal-tar dyes. What the child of Lebon suffered in one direction from the more sturdy growth of Murdoch's youngster, it gained in another from the partnership. Lebon fitted up his first retort in the back-yard of his father's house, conveying the gas to water-washers and thence to an inverted vat as

gas-holder. Like Murdoch he met with ridicule when he told his friends he would convey light and warmth from Paris to Brachay. Yet Fourcroy encouraged him, particularly when he began experiments on a larger scale at his house in the deserted grass-grown area of the Ile St. Louis, which had suffered much in days of the Revolution. Here he came on frequent visits while engineer at Charente in Angoulême. He met the charge of his superior officer that he visited Paris too frequently by pointing out the importance of his process to France. In 1796 he was granted patent rights for a process *Pour distiller au moyen du Vide et du Froid* ; three years later came his report to the Institut and his patent describing "*Moyens Nouveaux d'employer les Combustibles plus utilement et à la Chaleur et à la Lumière et d'en recueiller les Divers Produits.*" Despite all criticism Lebon continued with his fanatical faith in wood-gas. To meet objections to products of combustion escaping into the room in lighting, he introduced his "thermo-lamp" with tubes for admitting gas and air and a third one for leading off combustion gases. In his house in the Rue St. Dominique he exhibited a large thermo-lamp distributing both light and heat, and illuminated his garden by gas-jets. He was flogging a dead horse where lighting was concerned ; for he failed to obtain subscriptions for 200 of such lamps which he proposed to make. (Paris was still illuminated by oil lamps as late as 1837.) But the manufacture of wood-tar for the French marine took up his energies, after the granting of a concession over a large stretch of forest near Havre where he set up his wood-tar factory.

Meanwhile Murdoch, also beginning with an iron retort set up in a backyard, became father of the coal-gas industry and recipient of the Rumford Medal with appropriate inscription : *Ex fumo dare lucem.* There had been before his day one or two experiments on coal carbonisation. There was that early sniffing at a "Spirit of coals" described in a letter to the Honourable Mr. Boyle by the Rev. J. Clayton, D.D., an experiment which must have been made in the latter half of the seventeenth century before Boyle's death in 1691. Clayton, after noticing the water in a Wigan ditch "seemingly burn like brandy," found some coal below, distilled it in some crude form of retort, and obtained first a "phlegm," then a black oil, and also an uncondensable spirit. Coal had been coked at an ironworks abroad before Murdoch's work, yet no one had troubled to investigate when gases from the retorts became ignited. And there was a third experiment on the lines of Clayton's effort, this time by that Richard Watson who became a bishop but should have remained a chemist. Watson, appointed to the chair of

chemistry at Cambridge, though he frankly admitted " he had never read a syllable on the subject nor seen an experiment," was ever enquiring into fermentation, balsams, precious stones, the recovery of sulphurous fumes from lead-smelting, and other varied subjects. And though in 1786 he destroyed many chemical MSS. as " a sacrifice to other people's notions of the proper occupation of a church dignitary," there is a record of his distilling 96 ounces of Newcastle coal in an earthen retort, obtaining an " elastic vapour," and seeking to find what liquids, tar, residuum and loss in weight were to be noted on distilling other coals and wood.

Such experiments were mere curtain-raisers to Murdoch's work in gas-lighting in the 1790's, in face of much opposition. His initial effort at Redruth, described by Sir Joseph Banks to the Royal Society (*Phil. Trans.*, 1808), used wood and peat as well as coal from different localities, his iron retort having tinned copper and iron tubes attached for conveying the gas " to a considerable distance." This idea of piping the gas, as with Lebon, differentiates even those initial efforts from the dabblings of Clayton and Watson. As gas-burner he tried various nozzles, one example being a perforated thimble sent for, it is believed, via one of several small boy spectators who had their noses flattened to the window in admiration of these strange experiments. (The lucky one is believed to have wormed his way into the sanctum before the thimble could be extracted from his pockets.) Round about 1796 Murdoch, confident of the value of gas as illuminant, tried in vain to persuade Boulton and Watt to take out a patent. " I am persuaded I can either cure him of the disorder or turn the evil to good " : such was an example of Boulton's attitude, on this occasion when he met Murdoch near Exeter *en route* to London in his " steam carriage " and persuaded him to return. And so with gas-lighting in which Murdoch's enthusiasm had also to be restrained. Boulton and Watt considered they had enough lawsuits over Watt's patents to last them a lifetime. The opposition to " light without a wick " was to continue throughout Murdoch's large-scale success and beyond it to Winsor's efforts. " There is a madman here proposing to light London with smoke," was the sardonic comment of Sir Walter Scott. Humphry Davy asked if St. Paul's dome would be of use as gas-holder. Gas-lighting as target for the wit of littérateurs was seized upon, as were other new discoveries in the electrical and medical fields :

> What varied wonders tempt us as we pass !
> The cowpox, tractors, galvanism and gas,
> In turns appear, to make the vulgar stare,
> Till the swollen bubble bursts and all is air.

But Murdoch's obstinacy won through. Back at Soho in 1798 from a Scottish visit, he "constructed an apparatus upon a large scale, which during many successive nights was applied to the lighting of their principal buildings and various new methods were practised of washing and purifying the gas." In 1802 in celebration of the Peace of Amiens he dazzled a great crowd with a special display; in 1805 gas-lighting went further afield than Birmingham when a Manchester spinning firm adopted it.

Ex fumo dare lucem. That salute to Murdoch is to a man who brought 150 years ago a practical meaning to *Lux in tenebris*, who gave us modern lighting, which would be leading to-day had not Swan and Edison stumbled on the filament lamp. Murdoch has been served better at the hands of posterity than has Lebon; indeed, on some occasions his champions have been moved to excessive zeal—as in the case of that Shah of Persia visiting London in 1873, who learned with surprise the name of the inventor of gas-lighting, identified him with Merdoch, the God of Light of Assyrians, Babylonians and Persians, and ordered portraits of William Murdoch to be enshrined in Persian palaces. One assesses Murdoch's achievement by recalling Faraday's dictum and the list of crude illuminants before coal-gas came: the skull of burning fat; crude lamps of stone or clay; rough vessels of bitumen in the Far East; whale oil, seal oil, tallow; the tapers of oiled rope which lighted Tut-Ankhamen's tomb; wax-impregnated sticks; the modern candle which followed the work of Cabacières and Chevreul; and the Argand burner when a Geneva physicist was inspired to put a draught of air up the centre.

As postscript one must include a word for Welsbach, whose later discoveries not only rescued gas-lighting from extinction in face of electric lighting, but represented yet another jump in that scale of civilisation begun by Faraday. Auer von Welsbach differed from Lebon and Murdoch in being very much a chemist, a product of the Vienna Polytechnic and student of Bunsen, and discoverer of praseodymium and neodymium. In 1880, while studying the rare earths and finding small beads on a platinum wire hardly suitable for luminous spectra, he soaked cotton in his salts, calcined the mass, noticed the intense light, and began to investigate the possibilities of retaining coherence on the part of the skeleton ash. Oxides of lanthanum and magnesium proved almost useless; zirconia was found to have a life of a hundred hours; and finally thoria was tried with partial success after Welsbach had had to close down his small factory and set to work alone. After the purest thorium had given less valuable results, the mixture of

99 per cent. thoria and one per cent. ceria proved the answer for the Welsbach mantle. Welsbach, in memory of his early struggles with Latin, adopted *plus lucis* as his motto. And after this bringing of new life to Murdoch's progeny, what more fitting addendum to his work than the invention of the automatic flint gas-lighter, an invention coming after he had seen manufacturers giving away one pound of cerium salts with every 99 pounds of thoria, and after he had noted with dismay the accumulation of cerium residues on his factory dump ?

RECENT ADVANCES IN SCIENCE

ASTRONOMY. By. A. HUNTER, Ph.D., F.R.A.S., Royal Observatory, Greenwich.

METEORS AND RADIO.—Meteor observation is traditionally a matter for amateurs. Two circumstances have combined to make this so: the work is visual and ordinarily needs only the simplest of equipment; and it calls for a thorough knowledge of the constellations, which is rarely acquired by the professional astronomer. The latter, engaged as he usually is nowadays on a long-term programme of photographic observations with a big telescope, fails to see the wood for the trees, and as a result seldom knows the sky as well as his amateur colleague. This is not to say that the study is entirely neglected at the bigger observatories, but the work there is usually confined to photographing predicted radiants of meteor showers with wide-angle, short-focus lenses, or to track determination from cameras set up at the two ends of a measured base-line.

Two recent developments have brought the radio physicist into the field. Each of these was fortuitous in the sense that, though it opens up a new method of observing meteors, it was not the result of a deliberately designed attack on the subject. In the first, a meteor entering the atmosphere produces an audible whistle in an ordinary short-wave radio receiver situated in the neighbourhood of an antenna transmitting only a carrier wave at the time. The second method detects, by the standard radar technique developed during the war, the ionised trail left by the meteor in the upper atmosphere.

The first detailed mention of "whistling meteors" appears to be in a paper by S. R. Khastgir (*Indian Journal of Physics*, **17**, 239, 1943). It seems that weak whistles of rapidly descending pitch have been heard at the Delhi receiving centre of All-India Radio, located at a distance of 10 miles from the short-wave transmitters, when a receiver is tuned to the unmodulated carrier wave of one of the transmitters. They last from a fraction of a second up to a few seconds, and occur at random time-intervals. These whistles are attributed to the following mechanism: A meteor

entering the Earth's atmosphere is supposed to produce a rapidly moving mass of ionised air at its head. This local Heaviside layer scatters the incident short-wave radiation from the transmitter, the rapid descent causing a Doppler change of frequency in the scattered waves. These then interfere with the ground waves of unmodified frequency reaching the receiver by the ordinary path, and produce an audible heterodyne or beat note. As the descent is retarded by atmospheric resistance, the Doppler change of frequency lessens, and the pitch of the whistle descends. If an initial beat frequency Δn is superposed on an unmodified frequency n by a meteor of velocity v, the relation

$$\Delta n/n = 2v/c$$

should hold, c being the velocity of light. On a carrier wave of 7 Mc./sec., a whistle starting at (say) 3000 c./sec. would result from the entrance of a meteor with a maximum component of velocity towards the receiver of 64 km./sec., not an unreasonable value. The matter would seem to be clinched by the following facts: the whistles often coincide with visible meteors; they occur most frequently in the early morning, when the number and velocity of meteors is a maximum; and simultaneous whistles are heard on adjacent receivers tuned to different wave-lengths, the pitch of the whistles being proportional to the carrier frequency employed. But certain doubts of the validity of the Doppler explanation cause Khastgir to put forward another hypothesis which fits the facts equally well. In this, it is supposed that the retardation of a meteor in the ionosphere produces an electrical impulse analogous to audio-frequency static. The Fourier components of this impulse, transmitted at different velocities owing to the dispersive action of the ionised gas, will reach the lower boundary of the layer one after another in quick succession, the short waves arriving earlier than the long ones. The carrier waves scattered from the ionosphere will be modulated by the audio-frequency oscillations, the modulation frequency being a function of time, and a receiver tuned to the carrier will reproduce a descending whistle. The pitch of this whistle will be expected to depend on the carrier frequency, and its rate of fall will depend on the amount of dispersion, *i.e.* of ionisation. Test experiments can doubtless be devised to distinguish between the Doppler explanation and the modulation theory, but the astronomer will be primarily concerned, not with the detailed mechanism involved, but with the fact that here is a powerful new weapon at hand, which in some respects might almost have been designed to settle some of the very points about which visual observations

necessarily speak with uncertainty—notably the magnitude of meteor velocities.

The second method referred to above, using radar technique, has been developed by the former Army Operational Research Group (now under the Ministry of Supply) from the combined transmitter-receiver of 150 kW. peak power, used during the latter part of the war for following German high-altitude (V2) rockets. Pulses of 5 m. radiation are emitted from a transmitter antenna of which the bearing and elevation are adjustable. Radiation of this wave-length will, of course, penetrate the ionosphere whatever the time of day, season, or epoch during the solar cycle and whatever the angle of incidence. From localised patches of intense ionisation, such as the trails produced by meteors, however, echoes will be returned to appear on the cathode-ray tube of the receiver as "blips" whose displacement from the origin corresponds to the echo delay and thus to the distance of the trail, and whose persistence (seconds or even minutes) measures the time taken for recombination processes to reduce the ionisation in the trail below the critical value for reflection. Short-lived echoes are continually noted with such apparatus from a height of 90–100 km. and at an average rate of about ten per hour. When night observations with a vertically directed beam are made simultaneously with a visual watch for meteors, it is noticed that meteors passing nearly overhead give strong reflections. The deduction is that, as might be expected, the trails of ionised gas present their maximum echoing aspect when viewed at right angles to their length. Only about one echo in eight could be associated with a visible meteor, but this is doubtless because the brightness of the other seven fails to reach the naked-eye threshold. A graph of the mean hourly rate of occurrence of echoes picks out with certainty the known meteor showers such as the Quadrantids and Leonids, which appear as sharp peaks rising above the general level of echoes due to sporadic meteors (Hey and Stewart, *Nature*, **158**, 481, 1946). It is even possible, by observing with several inclined beams set on different bearings and utilising the aspect-sensitivity of the echoes, to determine within a few degrees the radiant of the shower concerned. While no great accuracy can be expected from this method, the hourly counts by themselves will be of great value to meteor observers, obtained as they are by a method independent both of cloud and of daylight.

The radar equipment was given a full-dress trial on the expected meteor shower associated with Comet Giacobini-Zinner and predicted for the night of October 9–10, 1946. This comet (1946c),

discovered by Giacobini in 1900 and recovered by Zinner in 1913, has a period of only six years and was first photographed on its latest return on May 29, 1946, at the Lick Observatory, very close to its predicted position. Since the comet's first appearance in 1900, perturbations have increased the size of its orbit and decreased its eccentricity, thus bringing the descending node close to the Earth's orbit. A small meteor shower was first noticed at its 1926 return. In 1933 the Earth came within half a million miles of the orbit, but at a point which the comet had passed eighty days before; nevertheless, there was a spectacular four-hour display reaching 400 meteors a minute at its peak. The 1939–40 return was unfavourable: though the difference between the orbits was smaller by a factor of four, the Earth passed the node over four months before the comet in 1939 and over seven months after it in 1940. The 1946 apparition was very much more hopeful than any previous ones: the Earth passed the node on October 10.1, only fifteen days behind the comet (then about 30 million miles away and, even at that, invisible to the naked eye) and within 135,000 miles of the orbit. Though of necessity little is known of the distribution of meteoric matter along the orbit, hopes ran high of a good display. Even if the peak were very sharp, the chances of visual observation were good in Europe and North America. As it turned out, however, observers in Western Europe, including the greater part of Britain, were almost entirely clouded out. Cloud spoiled the view from the eastern United States also, though from an aircraft above the clouds over Nova Scotia Harvard observers saw a display which included a meteor about as bright as Venus every few seconds. Professor Shapley is reported as saying that the shower was the richest show of the century.

The radar observers had nothing to fear from cloud. During the afternoon of October 9 the rate observed, ten per hour, was no more than expected from sporadic meteors. With little or no increase during the evening we have the radio observers' word for it that hard things were being said about the astronomers. But by midnight the hourly rate was up to 35, and at 4 a.m. on October 10, within an hour of the predicted maximum, a tremendous peak occurred. Echoes became too numerous to count, and final estimates of the frequency will have to await examination of the cinematograph records of the cathode-ray tubes. By sunrise the rate was down to normal again. Evidently the meteoric matter was confined very closely to the cometary orbit and was not, as with some other showers, observable many hours or even days on either side of the predicted peak. The evidence from previous returns of the comet

suggests that along the orbit too the concentration falls off rapidly away from the comet itself. It is perhaps a sign of advanced age in a periodic comet when the associated meteor shower shows a broad peak with time, and occurs whatever the relative positions of Earth and comet are at the time the node is passed.

It is too early yet to assess the full possibilities of these new methods of studying meteors. In the immediate future it may turn out rather that the radio physicists will be using meteors as ionosphere probes than that the astronomers will be employing radio methods for investigating meteors. Afterwards, perhaps, the new techniques will take their place in astronomy beside the time-honoured visual and photographic methods. If so, they will have some very definite advantages over the older techniques. The radar method gives a direct estimate of distance from a single observation—a great advance over the tedious method of photographing with twin cameras at either end of a measured base-line. The short-wave radio method gives meteor velocities (or at any rate line-of-sight components of velocity), over which there has long been controversy whilst only visual and photographic observation have been available. And both methods have the inestimable advantage of making observations possible in a cloud-covered or daylit sky. On the other hand, their resolving power is relatively low, and where determination of radiants is concerned, visual and photographic methods are not likely to be supplanted. It seems, in fact, that the techniques are complementary; the new methods will prove useful in just those aspects of meteor observation where existing methods have of necessity left aching voids.

Photoelectric Photometry.—Since the pioneer days of the early twentieth century, when the selenium cell was first used to measure the intensity of moonlight, photoelectric photometry has played an essential rôle in astrophysical technique. While not nearly so widely used for general photometry as the photographic plate, the photoelectric cell (which quickly supplanted the selenium cell) soon established itself in such applications as the accurate determination of light curves of variable stars, or (with suitable filters) the rapid estimation of star colours. The great disadvantage of the photocell is that it is not an integrating photometer, as is the photographic plate, so that in its practical application, backed by an electrometer rugged enough to stand up to the changes of position, temperature and humidity encountered during a night's observation, it is relatively insensitive. Nor, of course, does it make its own record, to be deciphered in comfort later and stored away for future reference, should that prove desirable. The introduction of the

electronic amplifier improved the sensitivity of the photocell, and enabled the much more convenient galvanometer to be substituted for the electrometer; but in its turn the amplifier introduced extraneous shot-noise masking the faint signals of the cell at low levels of illumination. Extremely sensitive photo-surfaces with very low dark currents have, however, been developed: the potassium hydride cell will yield 2×10^{-11} amp. with a fourth magnitude A0 star at the focus of the Mount Wilson 60-inch telescope, with a dark current of only 10^{-16} amp. At some sacrifice of performance the caesium oxide cell, yielding 3×10^{-12} amp. under the same stimulus, with a dark current of 4×10^{-15} amp., is sensitive over the wave-length range 3300–12,500 Å., though refrigeration with solid CO_2 and evacuation of the whole space containing cell and amplifier are necessary. With this latter cell, colour measurements can be made over the whole range down to 9·0 visual magnitude (Stebbins and Whitford, *Astrophysical Journal*, **98**, 20, 1943). Nevertheless, the introduction of the vacuum-tube amplifier has meant a sacrifice of efficiency to convenience, and anything which will achieve a higher signal-to-noise ratio will constitute a great advance.

This has now become possible with the wartime development of the electron multiplier. When the primary electrons in this device originate photoelectrically, the resulting "multiplier phototube" becomes essentially a photocell backed by a noise-free amplifier within the same glass container. The factor limiting performance is the primary shot-noise of the photocurrent and not, as with an external amplifier, the extraneous noise in the grid circuit of the amplifier. Without the use of impractically delicate laboratory apparatus—and it must be remembered that for astronomical reasons the nearer the conditions inside a telescope dome resemble the open air the better the astronomer likes it—the signal-to-noise ratio can now be pushed up from about 60 for the long-range CsO-Ag cell or 700 for the "quietest" cell (the K-H Kunz cell) to 10,000 or 20,000 with a nine-stage Sb-Cs photomultiplier (Kron, *Astrophysical Journal*, **103**, 326, 1946). Astrophysicists now have available in this latter device a photoelectric photometer which is about twenty times more sensitive than any heretofore used. With this multiplier operated from a voltage supply consisting of small hearing-aid batteries, a small simple D.C. amplifier and indicating meter enable satisfactory deflections to be observed on 16th magnitude stars with a 36-inch telescope. With an even simpler technique, employing a galvanometer in series with the anode circuit of the phototube, the 11th magnitude can be attained.

Without further refinements in present technique, then, such a multiplier at the focus of the biggest telescope in the world, the 100-inch reflector on Mount Wilson, will reach within two magnitudes of the limit attainable with the longest practicable exposure on a photographic plate. Considering that the apparatus is as yet in its infancy, it is permissible to look ahead with Kron to future possibilities of an ideal multiplier used under ideal conditions. This device will have a quartz envelope (for ultra-violet transparency and high electrical resistivity) with the anode lead brought out at the top to avoid leakage. (With the present nine-stage amplification, at 90 volts per dynode and 45 volts on the anode, a potential difference of 855 volts exists between adjoining socket pins on the base, and much of the output dark current is due to leakage across the base.) Its cathode area will be one-fifth that of the present tube, so as to reduce the dark current by a factor of five whilst still retaining the power to receive the whole of the light from a star or nebula. Operating at the temperature of solid CO_2, the cathode dark emission will be only about one electron per second. A star at the photographic threshold of the 100-inch mirror will give a photo-current of about 20 electrons per second, which will be multiplied up in three or four stages, each with an amplification factor of 12, so that the final anode output can be measured by a pulse-counter set to respond only to pulses of the right amplitude. Secondary electrons emitted spontaneously from the intermediate dynodes will not be amplified enough to trigger the counter. Dark-current electrons from the primary photo-surface which have gone through the whole of the amplifying labyrinth cannot be avoided, but they will be only about five per cent. of the total counted even at this low illumination level.

This conception of a photoelectric device measuring in a minute or so the radiation from stars as faint as or fainter than the faintest attainable photographically with exposures of hours may be a dream of the future, but such dreams have a way of coming true, especially when the apparatus on which they are based is developed under stress of war. Even now, as a result of wartime research, the astrophysicist has available a device which either will give him, without special precautions, as much sensitivity as he could get previously from the most sensitive photocell, with all the associated paraphernalia of vacuum pumps, refrigeration and sensitive electrometers or galvanometers; or will enable him, with a rather more specialised technique, to push his brightness threshold down by about three magnitudes. Swords into ploughshares indeed!

PHYSICS. By F. A. Vick, O.B.E., Ph.D., F.Inst.P., The University, Manchester.

Thermionic Emission from Oxide-coated Cathodes.—The number of electron tubes containing oxide-coated cathodes made each year must now amount to many millions, but the precise mechanism of the emission of electrons from such cathodes is still not completely understood. The processes for making the cathodes commercially are largely empirical and troubles arising during manufacture are cured, in many cases, by trial and error.

Most oxide-coated cathodes are prepared in the factory by mixing finely ground carbonates of barium and strontium with a binder, and coating nickel or other metal tubes, strips or wires with the mixture by spraying or deposition from the liquid. The proportion of $BaCO_3$ to $SrCO_3$ varies from one specification to another, but the double carbonate $(BaSr)CO_3$ seems to be becoming popular. The dried cathode is mounted in the electron tube, which is evacuated in the usual way. The cathode is then heated, to drive off the binder and convert the carbonates to oxides, the emitted gases being pumped away. The coating is "activated" by further heating, usually with the anode at a positive potential to draw an electron current from the cathode. At the end of this process, the oxide coating is found to be an efficient thermionic emitter. A typical cathode for a wireless receiving valve will emit about 100 mA per sq. cm. at 1000° K, or about 20 mA per watt of heating power. A pure tungsten filament has to be raised to about 2300° K to give the same emission, and its emission efficiency is then only about 1 mA per watt. If the coating is on wire or strip, the cathode is directly heated, but oxide coatings are particularly suitable for indirectly heated cathodes, consisting of a metal tube coated externally and heated from the inside by a separate filament insulated electrically from the tube.

The electron theory of metals, as modified in the light of quantum statistics, is able to account quantitatively for the measured thermionic emission from clean metal surfaces, and its temperature dependence. For adsorbed films of electropositive or electronegative atoms on metal surfaces, there are still some features not completely explained. For oxide-coated cathodes, rival theories have been the subject of controversy for perhaps twenty years, and "the influence of unforeseen factors has led to the accumulation of a mass of conflicting evidence and to the general conclusion that the mechanism of activation of an oxide-coated cathode is a complex one."

This quotation is taken from an article by J. P. Blewitt (*J. Appl.*

Phys., **10**, 668–79 and 831–47, 1939), which gives a very good summary of work carried out until the outbreak of war, with a fairly complete bibliography. There were two rival theories on the origin of the thermionic emission in oxide cathodes. The first considered the final electron current to be determined by emission from the core to the oxide, the electrons then being conducted through the oxide and emitted from its surface over a potential barrier having comparatively little influence on the emission. Evidence advanced in support of this theory included the discovery of barium in the core of aged cathodes (Lowry, *Phys. Rev.*, **35**, 1367, 1930), and deductions from the shapes of oxide conductivity curves (Reimann and Murgoci, *Phil. Mag.*, **9**, 440, 1930). Some years before, Koller (*Phys. Rev.*, **25**, 671, 1925) had suggested that the activity of oxide cathodes is due to a thin film of alkali metal atoms (Ba, Sr, etc.) on the surface of the oxide. This was developed by Becker (*Phys. Rev.*, **34**, 1323, 1929) and others into the second theory, which placed the emphasis on the potential barrier at the oxide surface, the characteristics of the emission from core to oxide playing a minor part. It is easy to show that alkali metals (mainly Ba) are evaporated from a hot oxide cathode on to a neighbouring cold tungsten filament, thus changing the thermionic emission from the latter. Becker demonstrated that an oxide cathode which has had barium deposited on its surface is activated with much the same result as by the treatment outlined above. The normal process of activation has been shown to produce free Ba (and Sr) not only at the core-oxide interface and at the oxide surface, but also dispersed through the body of the oxide. Becker postulated that during the life of the cathode some of the current passing through the oxide is carried by Ba and Sr positive ions moving electrolytically towards the core, and negative oxygen ions towards the surface. It is well known that oxygen is emitted from such a cathode during activation. The Ba film at the surface is maintained by diffusion. A crucial experiment which was thought at the time to disprove the first theory was carried out by Becker and Sears (*Phys. Rev.*, **38**, 2193, 1931), who dislodged by mechanical shock the coating from an active cathode and found that the emission had decreased by a large factor (over 1,000). If the core had been the original source of activity, they argued that the emission should have remained constant or even increased after the removal of the oxide. T. J. Jones (*Thermionic Emission*, p. 82, 1936) detached only the outer surface of the oxide layer (in vacuum) leaving the core-coating interface undisturbed. This caused its activity to fall to one-thousandth. Subsequent activation renewed the emission,

presumably by the formation of a new layer of Ba at the exposed oxide surface. These and other experiments seemed to relegate the rôle of the core to assisting in the dissociation of the oxides to provide dispersed Ba and Sr. That was the position at the time of Blewitt's 1939 review.

During the past few years interest has been stimulated by two factors; the realisation of the importance of the properties of the oxide as an excess semi-conductor, and the war-time use of oxide cathodes for the generation of pulses of emission rather than steady currents. It was found that the peak saturated current drawn in pulses of microsecond duration was many times (*e.g.* 100) the normal steady saturation current for the same cathode temperature. Time changes in saturation current had been observed before, and were discussed by Blewitt in the review cited above. They were not troublesome in practical electron tubes, however, because in such tubes the anode current is usually space-charge limited and the cathode is kept at constant temperature. During the war, however, the use of oxide cathodes in valves for pulse work drew attention to the enhanced emission and the time changes, and led to renewed study of emission properties of cathodes under such conditions. We are not concerned here with war-time applications, but the behaviour of oxide cathodes under pulse conditions should throw further light on the physics of the emission processes.

In a recent paper (*Phys. Rev.*, **67**, 166–78, March 1945) R. L. Sproull studied the current decay characteristics of oxide-coated cathodes, and the dependence of decay time and enhanced emission on the properties of the oxide coating. The experimental tubes used were sealed-off cylindrical diodes. Valve circuits were developed to apply a positive potential to the anode as suddenly as possible so that the thermionic current increased to its temperature-limited value in a small fraction of a microsecond. The changes in thermionic emission were recorded while the anode voltage was kept on for times varying between 100 and 2000 microseconds, and then switched off for a time long enough for the cathode to recover, and the process repeated. He found that on switching on the anode potential, the saturation current rose to an initial high value, and then decayed to a steady value one-fifth to one-fifteenth of the initial one. The rates of decay were proportional to current density, but independent of the thickness of the coating. In order to explain his results, Sproull suggests that as soon as thermionic current starts to flow through the oxide, the concentration of the alkali-metal layer at the surface commences to decrease from its equilibrium value by electrolytic movement through the oxide, thus

increasing the effective work function of the surface. The current decay curves seemed to be of the correct form as predicted by this hypothesis. The steady-state current increases as the size of the oxide particles decreases, as found previously. There is no space here to discuss the details of this provocative paper.

More recently, a paper has appeared on "The Pulsed Properties of Oxide Cathodes" by E. A. Coomes (*J. Applied Phys.*, **17**, 647–54, August 1946). He emphasises the following points, among others: (*a*) a good d.c. oxide cathode is not necessarily a good pulse-cathode; (*b*) when large currents are drawn in pulses from oxide cathodes there is, in general, a large rise in temperature of the cathode; (*c*) a major limitation on the maximum pulse current which can be drawn from the cathode is the onset of sparking, *i.e.* the physical transfer of particles of the cathode to the anode; (*d*) the effect of the base (core) metal on pulse properties may be considerable. Pure nickel seems the best for pulse cathodes. Coomes suggests a different reason for the enhanced emission during pulses from that advanced by Sproull, namely that electrons in the excess semi-conductor (*i.e.* the oxide) thermally excited into the conduction band during the period between pulses is swept out during the pulse, adding to the normal thermionic emission for a short period. (The normal space-charge in the inter-electrode space in a valve may be shown to contribute an amount small compared with the normal peak pulse emission.)

A. Eisenstein has contributed two papers on the study of oxide cathodes by X-ray diffraction (*J. Appl. Phys.*, **17**, 434–43, June 1946, and **17**, 654–63, August 1946). Since barium and strontium oxides are unstable in an atmosphere containing CO_2 and water vapour, special techniques were necessary to examine activated cathodes, and these are described in the first paper. In some cases the cathodes were covered by a protective layer while in dry nitrogen and then removed from the tube, and in others they were examined when in a vacuum, the primary and diffracted X-ray beams passing through beryllium windows. The first study reported is that of the conversion of the carbonates to the mixed oxides of an activated cathode, with particular reference to the solid solution in equi-molar proportions $(BaSr)CO_3$. X-ray diffraction patterns were obtained during the three main stages of conversion, (i) crystal growth in the carbonates; (ii) decomposition to oxide and solid solution formation; (iii) crystal growth in the oxides. The crystal size of the resultant oxides appeared to be unrelated to the initial carbonate crystal size. The oxide crystal size depends mainly on the maximum temperature reached during the processing.

The second study was a determination of the change of lattice dimensions of oxide crystals with temperature, that is, the thermal expansion coefficient. This factor is, of course, important in the adherence of coatings to the core.

In his second paper, Eisenstein describes investigations of the changes with life of a cathode, initially equal molar (BaSr)O. A method of calculation was devised which allowed an estimate of change of oxide composition with depth to be made. It had already been shown by a number of investigators that near the surface of a cathode towards the end of its life the lattice consists of SrO, the BaO having disappeared, and Eisenstein confirmed this finding. The effect of the material of the core on the loss of BaO from surface and bulk of the coating was studied, and detailed results are given of the change of composition with depth. The two papers are important contributions to our knowledge.

In another paper, Fineman and Eisenstein (*J. Appl. Phys.* **17**, 663–8, August 1946) apply X-ray diffraction methods to the study of the interface between core and oxide. The surface coatings of aged cathodes were scraped off in an atmosphere of nitrogen, the remaining coating covered with a protective layer, and examined. In addition, coating and interface resistances to microsecond pulses were measured by probes embedded in the cathode mixture during coating. Not all the compounds at the interface between the oxide coating and different cores were identified, but special interface patterns were found in all cases examined. The curves of interface resistance against current were of similar form to those exhibited by multiple-layer oxide rectifiers, and suggest that a rectifying barrier layer may exist there.

J. P. Blewitt has brought his review of literature up to 1945 (*J. Appl. Phys.*, **17**, 643–7, August 1946), and his paper contains the useful suggestion, due to Hahn, that the methods in Chapman and Cowling's book *The Mathematical Theory of non-Uniform Gases* be applied to the study of oxide-coated cathodes under non-equilibrium pulse conditions.

The considerations described above are leading to an extensive revision of our views on the mechanism of emission from oxide-coated cathodes. The working hypothesis used in the Manchester Laboratories for some time is also proposed by Coomes (*loc. cit.*) and has doubtless been evolved by other workers in the field. It is that an oxide-coated cathode consists of metal core + barrier layer rectifier + excess semi-conductor + potential barrier at the vacuum surface. The equilibrium value of thermionic emission depends, on this view, on *all* these factors. There is thus an approach to a

reconciliation of the rival theories described above. With this working hypothesis before us, together with a better understanding of the nature of semi-conductors, barrier-layer rectifiers, etc., the re-examination of previous work and the planning of new experiments should prove very fruitful. One such programme has been begun in Manchester.

METEOROLOGY. By P. A. Sheppard, B.Sc., F.Inst.P., Imperial College of Science and Technology, London.

Radiation in the Stratosphere and Troposphere

1. Introduction

In this series of articles we shall continue for some while to review progress in particular branches of meteorology since about 1939 to the time of writing. On this occasion the treatment will be on the rôle of radiation in meteorology, but we shall concern ourselves only with the atmosphere below about 50 km. which, readers may care to be reminded, consists of (*a*) the troposphere, from ground level to about 7 km. over the poles and 18 km. over the Equator, in which the temperature normally decreases with height at about 6° C. per km. and which contains four-fifths or so of the total mass of the atmosphere, (*b*) the stratosphere, separated from the troposphere by a usually sharp discontinuity of temperature-gradient termed the tropopause, above which the temperature is practically constant—it usually increases very slowly with height in the equatorial and mid-latitude stratosphere and decreases slowly with height in winter in the polar stratosphere, (*c*) an upper warm region ("empyrean" was the name suggested by Whipple) from about 35 km. to 50 km. or so, in which the temperature rises at about 5° C. per km., but about which little is known in detail, partly because it is outside the present bounds of direct exploration by sounding balloons. Although layers (*b*) and (*c*) are fairly distinct, it is probable that the temperature distribution within them both is the result mainly of radiation processes and the stratification being stable throughout we shall in the remainder of this article normally refer to them jointly as the stratosphere.

We shall consider in turn knowledge gained on the modification of solar radiation as it passes downwards through the atmosphere, and then of atmospheric and earth radiation as it passes out into space and of the reaction of these beams of radiation on atmospheric temperature. But before doing so some notice is required of recent work on the amount and distribution of the atmospheric gases which play a direct part in the radiation processes.

2. The Amount and Distribution of Absorbing Gases

(*a*) *Water Vapour.*—Water vapour is prospectively one of the most important gases in the radiation problems of the atmosphere, because of the wide range of its absorption bands from the near to the far infra-red; yet, until recently we could only guess at the quantities present in the stratosphere. This was due to the excessively large lag at low temperature of hygrometric materials, such as hair and gold-beaters' skin, which have been used on sounding instruments, the lag arising primarily from the necessarily exceedingly small, but not for that reason unimportant water-vapour content of air at low temperature. The position has, however, been lately revolutionised by the design and use of an aircraft frost-point hygrometer by Dobson, Brewer and Cwilong (*Proc. Roy. Soc.*, **185,** 144, 1946; see also Dobson and Brewer, *J. Roy. Aeron. Soc.*, **50,** 787, 1946). This instrument is capable of giving the frost point down to about 183° K, below which the ice is deposited in a vitreous form which escapes detection by normal methods, the error of observation being not more than 1° or 2°. Some 20 soundings have been made into the lower stratosphere of this country with the new instrument, a height of 12 km. having been reached, and all soundings showed a very dry stratosphere with relative humidities of a few per cent. only (frost points of about 190° K with air temperatures 30° to 40° higher). It would be dangerous to generalise from these few observations, but it is clear that the lower stratosphere in mid-temperate latitudes is generally very much drier than previously supposed by many meteorologists. If we assume that there is a constant mixing ratio of water vapour to dry air throughout the body of the stratosphere (see § 2 (*b*) below) with frost points as observed in its lower region, the amount of precipitable water in the stratosphere is of the order of 10^{-3} to 10^{-4} cm. only. These soundings have also shown exceedingly dry layers (relative humidity 1 or 2 per cent.) to exist from time to time in the troposphere after subsidence has occurred and, though they are shallow, they may be quite important for the change in temperature produced by radiative exchange (see § 4 (*b*) below). Such extremely dry layers may not be shown at all faithfully on routine radio soundings whose accuracy is, for these purposes, inadequate, though for seasonal or air-mass mean values of humidity of the lower and middle troposphere they are probably just about adequate.

Radiation problems normally require a knowledge of the vertical distribution of an absorbing gas, but the total quantity of gas above

a given level may be of interest in some instances, and techniques for this measurement for water vapour have been described by Hand (*Mon. Wea. Rev.*, **68**, 95, 1940) and Strong (*J. Franklin Inst.*, **232**, 121, 1941). Both make use of the absorption of solar radiation in well-mapped bands in the near infra-red, the former comparing the intensities of solar radiation in narrow adjacent bands, of which one lies in and the other outside the water-vapour band near 0·9 μ, the latter measuring the total absorption over the ϕ band (1·05 to 1·25 μ). Hand claims an accuracy of 0·1 cm. precipitable water, but Strong's accuracy is not stated; presumably it will be affected by the presence of dust and haze above the station.

(*b*) *Carbon Dioxide.*—The frost-point hygrometer referred to above can be used to measure the CO_2 content of air and it has been found that the proportion of CO_2 in the lower stratosphere is the same (0·03 per cent. by volume) as near the surface. This result is consistent with Paneth (*Quart. J. Roy. Met. Soc.*, **65**, 303, 1939) and Paneth and Glückauf (*Proc. Roy. Soc.*, **185**, 89, 1946), but the latter find evidence of slight diffusive separation of the lighter from the heavier gases between 20 and 25 km. The slight change in composition at these levels is not, however, likely to be significant for radiation studies involving either carbon dioxide or water vapour.

(*c*) *Ozone.*—Dobson, Brewer and Cwilong (*loc. cit.*) have considerably amplified our knowledge of the day-to-day variations in the total ozone content of the stratosphere. They find that the changes, up to about 30 per cent. of normal values, are mainly associated with the passage of fronts, a fall occurring ahead of most surface warm fronts and a rise immediately to the rear of surface cold fronts. Occluded fronts show variations dependent on their type. Some fronts, however, show no ozone variations, and it is inferred that these do not then reach into the stratosphere where most of the ozone is concentrated. Dobson considers that the ozone variations are mainly confined to the layer between about 10 and 20 km., a view consistent with the fact that mean ozone values are low in tropical and high in polar regions. We shall see later (§ 4 (*c*)) that these variations are very significant in relation to the temperature of the stratosphere and the height of the tropopause.

There has been no considerable advance in knowledge on the vertical distribution of ozone, but a new technique has been developed by Strong (*Phys. Rev.*, **55**, 1114, 1939; *J. Franklin Inst.*, **231**, 121, 1941), and Strong and Watanabe (*J. Franklin Inst.*, **236**, 461, 1943), for observing the mean atmospheric pressure and hence height of the ozone. The total amount of ozone is measured from

the absorption of solar radiation in the Hartley (*u-v*) band, while a simultaneous measurement of the absorption in the 9·7 μ band, which depends on the fourth root of the total pressure, leads to an estimate of the mean pressure. The technique is difficult and subject to several possible errors, but the mean heights observed, 20 to 28 km., are in rough agreement with the rather few results of earlier workers, and the method has the great merit of providing instantaneous values whose variation may be followed with an unobscured sun. No correlation of such variation with other meteorological factors has yet been made.

3. The Depletion of Solar Radiation by the Atmosphere

(*a*) *Stratospheric Depletion.*—The most complete recent treatment of this problem appears to be that given by Karandikar (*Proc. Indian Acad. Sci.*, **23**, 70, 1946), who evaluates the absorption of solar energy per unit volume and per unit mass in 2 km. layers below 50 km. by ozone, carbon dioxide and water vapour, for various solar elevations, using the latest data on absorption. He adopts a solar "constant" of 2·045 cal. cm.$^{-2}$ min.$^{-1}$ and a radiative temperature for the sun—to provide the energy distribution function—of 6000° K. These two values are slightly inconsistent, but that is of little consequence to the succeeding computations. These are based on graphical methods giving, first, the energy extracted in each absorption band and *in toto* as a function of path length through the gas considered, and, secondly, the distribution of energy absorption with height for given vertical distributions of the absorbing gases. He also uses a formal technique due to Chapman (*Proc. Phys. Soc.*, **51**, 93, 1939) as a check in certain regions and obtains good agreement with the graphical method. For ozone it is shown that above 30 km. the ultra-violet (Hartley) absorption far outweighs the absorption in the visible (Chappius) and infra-red bands, but that below 30 km. the Hartley and Chappius bands produce comparable absorptions, the latter band being the more important for large zenith distances of the sun. Taking all bands, the absorption above 20 km. far exceeds that below, while quadrature of Karandikar's curves shows that the total absorption down to 10 km. varies from 5·3 per cent. to 7·5 per cent. of the incident radiation for air masses 1 to 4 (air mass = secant of zenith angle) for an ozone distribution as observed at Tromsö.

The total absorption by carbon dioxide in the stratosphere, mainly in the 2·7 μ band, is very small compared with that of ozone, but the absorptions by the two gases are comparable in the lower stratosphere.

The absorption by water vapour is mainly confined to wave lengths less than 4 μ, the large absorption coefficients of water vapour at longer wave lengths being of little account due to the small solar energy in the longer waves. The actual amount of energy absorbed by water vapour remains uncertain, but Karandikar's curves taken in conjunction with the precipitable water deduced (§ 2 (*a*)) from Dobson et al (*loc. cit.*) suggest that it is negligible compared with that by ozone, except below 30 km.

Karandikar's compounded figures of total absorption for average solar elevations vary from about 1×10^{-4} cal. gm.$^{-1}$ min.$^{-1}$ at 15 km. to about $2{\cdot}5 \times 10^{-2}$ cal. gm.$^{-1}$ min.$^{-1}$ at 45 km. where there is a very sharp maximum. Quadrature of his curves gives 5·9 per cent. to 8·5 per cent. absorption of the incident radiation down to 10 km. for air masses 1 to 4, with an ozone distribution as at Tromsö and 5×10^{-4} cm. precipitable water, percentages only slightly larger than those given above for ozone only.

Karandikar's paper is the first of a series promising to deal also with the emission of radiation by the stratosphere and finally with radiative equilibrium temperatures. Anticipating this later work it is already clear from the values of solar absorption that there can hardly be any appreciable diurnal variation of temperature in the lower stratosphere, for if all the solar energy there absorbed were manifest as a rise in temperature this would be mainly less than 0·5° C. per day, a result of importance in judging the reliability of radiosonde temperatures taken at those levels in daylight. At higher levels, however, particularly between about 40 and 50 km., there must be an appreciable diurnal variation of temperature unless the absorption is matched by a rapid increase of atmospheric radiation with temperature.

(*b*) *Tropospheric Depletion.*—There are no absorbing gases present in the troposphere that are not also present in the stratosphere.[1] The absorption by ozone is effectively complete at the level of the tropopause, so that its presence (in very small amount) in the troposphere is of no consequence. For carbon dioxide this is not quite the case, and still less for water vapour, as may be inferred from Karandikar's curves. Hoelper (*Met. Z.*, **60**, 37, 1943) has given revised values of water-vapour absorption from the solar beam for tropospheric water-vapour contents which, the writer finds, can be accurately represented by A (cal. cm.$^{-2}$ min.$^{-1}$) $= 0{\cdot}118 \log_{10} w + 0{\cdot}133$, valid over a range of w (centimetre of precipitable water) from 0·5 to 8 cm., the actual values of the absorption at these extremes being 0·10 and 0·24 cal.

[1] With the exception perhaps of small quantities of the oxides of nitrogen.

cm.$^{-2}$ min.$^{-1}$ respectively. This absorption is then of the same order as that given above for the stratosphere, and Möller considers that its distribution is such as to produce an equivalent heating of about 0·5° C. per day more or less independent of height throughout the troposphere. But gaseous absorption in the troposphere is rather small compared with other agencies depleting the solar beam, such as reflexion from cloud tops, and absorption and scattering by dust and nuclei. For these we turn to a recent investigation of Haurwitz (*J. Met.*, **2**, 154, 1945) conducted on empirical lines, and to Hewson (*Quart. J. Roy. Met. Soc.*, **69**, 47 and 227, 1943) for a theoretical investigation of the action of clouds of water drops.

Haurwitz has analysed observations of total (direct and scattered) insolation received on a horizontal surface at Blue Hill Observatory, Massachusetts (elevation 195 m. above sea level) in terms of air mass, cloud amount and cloud density, the latter being estimated visually on a subjective scale of 0 to 4 (see *International Atlas of Clouds and States of Sky*, **1**, 59, 1932). The insolation, I, conforms well on the whole to an equation of the form $I = (a/m)e^{-bm}$, where m is the air mass and a and b constants which depend on the cloud amount and cloud density, though, as might be expected, individual observations show large departures from the mean curve. For example, even with clear skies atmospheric turbidity exercises a marked control on the insolation. Table I summarises the actual observations in certain classes (a misprint in the original paper has been corrected) and Table 2 gives the values of a and b in the empirical representation.

TABLE 1

(figures in body of Table give Insolation on horizontal surface in cal. cm.$^{-2}$ min.$^{-1}$)

Cloud Amount (tenths).	0	1–3		4–7		8–9		10	
Cloud Density (0 to 4).	—	1	3	1	3	1	3	1	3
Air Mass 1·5	0·958	0·960	0·865	0·922	0·793	0·880	0·627	0·760	0·253
Air Mass 3	0·438	0·410	0·420	0·392	0·303	0·407	0·255	0·348	0·117

It will be noted that the effect of cloud density on the insolation is of about the same importance as the cloud amount if the sky is mainly or wholly covered, while for small cloud amounts the insolation, as might be expected, depends very little on the cloud density.

TABLE 2

(values of a and b in $I = \frac{a}{m} e^{-bm}$ cal. cm.$^{-2}$ min.$^{-1}$)

Cloud Amount (tenths).	Cloud Density (0 – 4).									
	0		1		2		3		4	
	a	b	a	b	a	b	a	b	a	b
0	1·57	0·059	—	—	—	—	—	—	—	—
1–3	1·81	0·160	1·69	0·105	1·60	0·094	1·33	0·018	—	—
4–7	—	—	1·63	0·110	1·61	0·152	1·56	0·179	—	—
8–9	—	—	1·43	0·055	1·20	0·072	1·15	0·137	—	—
10	1·35	0·047	1·25	0·061	1·05	0·154	0·52	0·134	0·27	– 0·007

The ratio of the insolation under cloudy and clear skies, *i.e.* the fractional transmission of a cloud, is given by

$$I/I_0 = \frac{a}{1{\cdot}57} e^{-(b-0{\cdot}059)m}$$

where I_0 is now the insolation under clear skies, so that for a given cloud amount and cloud density (given a and b) the transmission decreases with increasing air mass for $b > 0{\cdot}059$, which is mainly the case. But the variation of the transmission with air mass is in any case rather slight. Also of interest is the fact that the air mass is shown to be quite the most important factor controlling I except with an overcast (10/10) or heavily clouded sky when the cloud density exercises a comparable control.

The above figures and conclusions are strictly valid for the area of Blue Hill Observatory only, and then only on a statistical or climatological basis. In other parts of the world with air masses of different properties or different dust, smoke or nuclear contents there would no doubt be differences in detail, but the broad trend of the results is likely to be general.

Haurwitz's results are important for the many meteorological problems which require a knowledge of the amount of solar radiation reaching the ground, *e.g.* surface temperature and its variation, the formation and dissipation of cloud, agricultural and biological meteorology, etc., but it does not tell us in detail what happens to the radiation in passing through the troposphere. Hewson (*loc. cit.*) has made an attack on this problem as far as the effects of cloud and fog composed of water droplets are concerned. The problem is one both of scattering and absorption, and Hewson uses Mecke's equations for these processes to obtain the intensity of the upward and downward beams in the cloud. He takes Wiener's computed values of the scattering coefficient for water drops whose radii

are greater than the wave length of light concerned, and a value of $4/3rk$ (r = radius of drop, k = Naperian absorption coefficient of water at wave length λ) for the fractional absorption per drop. Kimball's observations of the distribution of energy with wave length in an average clear atmosphere, for various zenith distances of the sun, are used to provide the energy (direct and diffuse) incident on the upper surface of the cloud, while values are available for k as a function of wave length. Hewson neglects the effect of the direction of the solar beam on the upward and downward scattering of the cloud, all computations being made for a zenith angle of 67° for which the upward scattered light is the same as for diffuse light of the same total intensity. Strong criticism has been expressed at this procedure (*Quart. J. Roy. Met. Soc.*, **69**, 227, 1943), but Hewson advanced evidence that, except near the boundary of a cloud of very small water content or one composed of large drops, the radiation within the cloud is almost completely diffuse and its behaviour therefore mainly independent of solar elevation, though the intensity will, of course, depend on the zenith angle (see on this point: Middleton, *Visibility in Meteorology*, Toronto, 1944). Hewson's results are essentially numerical and he gives figures for the percentage reflection, absorption and transmission of radiation for fogs and clouds of various thickness and water content, assuming a fog to be composed of drops all of 20 μ radius and a cloud of drops all of 5 μ radius. Whether these figures are representative is still uncertain, for observations on the constitution of fog and cloud are still scanty and by no means free from objection on grounds of technique. Hewson uses Houghton and Radford's data on fogs (*Mass. Inst. Tech. Pap. Phys. Ocean. Met.*, **6**, 4, 1938) and Bricard's observations on clouds (*La Mét.*, **15**, 83, 1939). (We shall return to this subject in a later review.) Table 3 gives illustrative figures, all for a zenith distance of the sun of 25°, since only for a very dense, deep fog is there any effect of zenith distance.

It will be noted that the range of reflection and transmission is almost the maximum possible, whereas it has in the past been common practice to ascribe a constant albedo of 78 per cent. to all cloud tops, for lack of observations other than those of Aldrich taken on a single fog-top. For a cloud or fog of appreciable density and thickness, however, Table 3 gives the albedo as lying between about 60 per cent. and 90 per cent. Hewson's figures may not, unfortunately, be adequately checked at present against any sustained series of observations, but a very rough test of the transmission values may, at least, be made against Haurwitz's figures

TABLE 3

PERCENTAGE OF SOLAR RADIATION REFLECTED (R), ABSORBED (A) AND TRANSMITTED (T) BY FOGS AND CLOUDS OF STATED DEPTH AND WATER CONTENT.
(Sun's Zenith Distance = 25°)

Water Content g/m^3.	Depth (m).	Fog ($r = 20\mu$).			Cloud ($r = 5\mu$).				
		20	80	200	20	80	200	1000	4000
0·1. . .	R	1·4	6·0	12·6	6·6	18·8	37·9	73·4	88·6
	A	0·1	0·2	0·8	0·0	0·2	0·6	2·7	5·2
	T	98·5	93·8	86·6	93·4	81·0	61·5	23·9	6·2
1·0. . .	R	12·6	35·9	56·8	37·9	69·1	82·9	91·7	93·3
	A	0·8	2·6	4·8	0·6	2·4	4·0	6·0	6·2
	T	86·6	61·5	38·4	61·5	28·5	13·1	2·3	0·5
5·0. . .	R	41·3	69·9	81·1	73·4	88·6	91·7	93·3	93·6
	A	2·9	7·2	9·8	2·7	5·2	6·0	6·2	6·3
	T	55·8	22·9	9·1	23·9	6·2	2·3	0·5	0·1

quoted above. According to Table 3 the transmission of dense clouds (depth ≮ 1000 m., water content ≮ 1 gm./m.^{3}) is only about 2 per cent. or less, whereas Haurwitz's observed transmission through 10/10 cloud of density 3 or 4 is about 28 per cent. or 20 per cent. respectively. Only for very shallow clouds of moderate water content or for moderately deep but quite tenuous cloud does Hewson obtain transmissions as high as Haurwitz's values. The discrepancy appears, therefore, to be wide. Hewson's conclusion that the percentage transmission is almost independent of solar elevation is, however, fairly well supported by Haurwitz. It will further be noted from Table 3 that the absorption by fogs and clouds may amount to a few per cent. of the incident radiation, but even this low figure must be of importance in the conditions controlling the dissipation or development of cloud and fog. The table also shows that a fog reflects less and transmits more radiation than a cloud of equal depth and density, a result which is, indeed, to be expected on the basis of the assumed difference in drop size.

There appears to be no important recent research on the modification of the solar beam by other constituents of the troposphere, such as dust, though clearly this must be important on many occasions. Thus, bearing in mind the value of the solar constant and the rather small gaseous absorption of the stratosphere and troposphere, the first column of Table 1 shows how considerable is the non-gaseous absorption and scattering of the average "clear" troposphere. If the loss is primarily due to absorption by dust, as

seems likely, there will be an appreciable reaction on the temperature of the dust-containing layer when this is limited in thickness by stable conditions aloft. Hoelper (*loc. cit.*) has discussed the extinction coefficient (but not the absorption) of particulate matter of radius 0·1 to 1 μ, while Ramachandra (*Proc. Indian Acad. Sci.*, **17**, 171, 1943) has developed a wave theory for the transmission of light through suspensions of both opaque and transparent particles of diameter larger than the wave length. The latter author finds that the diminution of intensity in the forward direction is actually double that which would be expected on simple geometrical considerations.

4. Atmospheric Radiation

(*a*) *Absorption and Emission Laws for Gases in the Infra-Red.*—This subject has received wide attention in the last few years on account of the increasing importance of infra-red spectroscopy to the molecular physicist and to the analytical chemist, and the meteorologist has gained much as a result. A good general treatment of the absorption laws of gases in the infra-red with special reference to the interpretation of experimental data has been given by Nielsen, Thornton and Brock Dale (*Rev. Mod. Phys.*, **16**, 307, 1944), while Schnaidt (*Beitr. Geophys.*, **54**, 203, 1939), Callendar (*Quart. J. Roy. Met. Soc.*, **67**, 263, 1941), Elsasser (*Harvard Met. Studies*, No. 6, 1942), Cowling (*Rep. Phys. Soc. Prog. Phys.*, **9**, 29, 1943) and Callendar and Sutherland (*ibid.* 18) have discussed these laws in relation to water vapour, carbon dioxide, ozone and the oxides of nitrogen which are the active components of the atmosphere in the infra-red. No attempt to summarise these papers will be made here except to say that absorption by any band, or line of a band, in the infra-red does not in general obey Beer's Law, and that efforts have been directed towards providing working formulæ for absorption which will take the line and band structure adequately into account, particularly in respect of its dependence on the total pressure and temperature, whose effects however are not yet fully resolved. Cowling has given a semi-empirical form for the absorption A by a gas of optical thickness w at total pressure p in any wave band, for A is greater than about 10 per cent., *viz.* $A = \text{erf}\left\{\frac{1}{2}\beta\left(\frac{pw\pi}{p_0}\right)^{\frac{1}{2}}\right\}$, where p_0 is standard pressure and β is an absorption coefficient which takes account of the line and band structure in the wave band concerned. For moderate values of A the formula approximates to $A = \beta(pw/p_0)^{\frac{1}{2}}$. Cowling provides values of β for water vapour in the range 5 to 150 μ, though in certain parts of

the range the values are still tentative. Callendar has provided values of yet other semi-empirical absorption coefficients for CO_2, coefficients which depend on the wave-length intervals to which they are applied, while Callendar and Sutherland have given values of a semi-empirical coefficient for O_3.

Falckenburg (*Met. Z.*, **55**, 174, 1938 ; *ibid.*, **56**, 72, 1938), Brooks (*Mass. Inst. Techn. Pap. Phys. Ocean. Met.*, **8**, No. 2, 1941) and Elsasser (*loc cit.*, also *Mon. Weath. Rev.*, **69**, 1, 1941) have each published observations on the *total* radiation of columns of water vapour, or of water vapour and CO_2, or of CO_2 separately at normal pressures and temperatures. For a column of CO_2 the emissivity ε (in per cent. of black body radiation at the temperature concerned) is given closely according to Elsasser's analysis by $\varepsilon = 6{\cdot}8 \log_{10}x - 5{\cdot}4$, where x is the length (m.) of the column at S.T.P., valid over the range 20 m. $< x <$ 10,000 m., the corresponding range of ε being from 3 per cent. to 22 per cent. ; for a column of water vapour the corresponding formula based on Brooks' observations corrected for CO_2 content is $\varepsilon = 340w^{\frac{1}{2}} - 2{\cdot}0$, where w (cm.) is the precipitable water in the column, valid over the range 0·0001 cm. $< w <$ 0·0025 cm. and giving for ε a range from 2 per cent. to 15 per cent. These total-radiation formulæ are useful for approximate computations, but their limitations should be clearly appreciated, for which see Sheppard (*Quart. J. Roy. Met. Soc.*, **68**, 210, 1942).

(*b*) *Atmospheric Radiation in the Troposphere.*—Elsasser in his 1942 paper describes a radiation chart (a revision of an earlier chart) based on his analysis of the water-vapour spectrum and on his observations of total radiation. This chart ideally enables one to compute the upward and downward flux of radiation at any level in the troposphere, given the distribution of temperature and vapour pressure as a function of the pressure (height), and the level and temperature of black-body surfaces (ground surface or cloud-sheet boundaries). That part of the flux due to CO_2 is assumed to be determined solely by the temperature at the level in question. The difference in net flux at any two levels can then be readily deduced, from which the rate of radiative heating or cooling in the layer immediately follows. Elsasser (*Mon. Weath. Rev.*, **68**, 185, 1940) using the first edition of his chart confirms earlier deductions of Möller that the troposphere is everywhere cooled by atmospheric radiation, in other words that the net upward flux increases everywhere with height, which is mainly a consequence of the rather rapid decrease of the downward flux with increase of height, as the water vapour, the chief radiator, is rapidly left below. The cooling

is more in equatorial than in polar air masses, and more at low levels than at high, but the actual amount of cooling for a given temperature and water-vapour distribution remains rather uncertain, perhaps 0° to 2° C. per day depending on the level and the air mass. (In 1940 Elsasser gave : rate of cooling (° C./day) $= 1 + 2 \log_{10} q$, where q is the specific humidity in gm./kg. at the level considered, but the 1942 revision of his chart implies that this is an over-estimate). We note that atmospheric radiation has a stabilising influence on the atmosphere since it causes less cooling above than below, but only when turbulence in the free atmosphere is relatively slight is the differential cooling by radiation likely to modify seriously the pre-existing temperature profile.

Brooks (*loc. cit.*) remarks that his curve of emissivity versus path length may be used quite simply in conjunction with a curve of temperature versus weighted water-vapour content to compute the atmospheric radiation and, at the present state of knowledge, this method is probably as satisfactory as any for dealing with the troposphere. Neither Elsasser nor Brooks take account of ozone radiation, which arises mainly in the stratosphere, but this is of no consequence for most purposes in the troposphere, since the ozone radiation is hardly modified in its downward passage through the troposphere.

Möller (*Beitr. Geophys.*, **58**, 11, 1941) has discussed the effects of atmospheric radiation at discontinuities of water-vapour content and of haze. His methods are not quite in line with modern knowledge on the laws of gaseous infra-red absorption, but his results are probably correct as to order of magnitude. Thus at a level of a sudden drop in water-vapour content, such as may exist at a subsidence inversion, he finds that the radiative cooling may amount to about 7° C./day, falling rapidly in amount both above and below the discontinuity. If there is thick haze below the discontinuity and clear air above, as often happens, the rate of cooling at the discontinuity may rise to about 14° C./day, again with a rapid decrease below and above. These results are for normal temperature lapse or isothermal conditions. A temperature inversion of 2° C. at the vapour-haze discontinuity will, however, reduce the cooling to about 8° C./day. Even so the cooling is very considerable and more than sufficient to account for the formation of cloud sheets such as frequently occur at discontinuities of these kinds.

Falckenberg and Hecht (*Met. Z.*, **58**, 11, 1941) describe the results of measurements of the downwardly directed beam of atmospheric radiation made from an aircraft up to a height of 1 km. They find the decrease in intensity with increase in height to be much

less than that given by Ångstrom's empirical formula relating atmospheric radiation to the temperature and vapour pressure at the level of observation.

(c) *Atmospheric Radiation in the Stratosphere.*—The absorption and emission of radiation in the troposphere, which have been considered in previous sections, are in general less important than vertical motion and condensation in determining the thermal structure of the troposphere. That is almost certainly not so in the stratosphere, which is often assumed to be the result of radiative equilibrium alone, *i.e.* radiation emitted at any level = radiation absorbed from the solar beam + radiation absorbed from upward and downward beams of terrestrial radiation. The test of this hypothesis is to determine whether the temperature of radiative equilibrium at all levels in the stratosphere is in agreement with observation, but this test cannot yet be thoroughly applied on account of our imperfect knowledge of the amount and distribution of water vapour and ozone present and of the absorption laws in the infra-red. A very striking advance has, however, recently been made by Dobson (*Quart. J. Roy. Met. Soc.*, **68**, 202, 1941) and his co-workers (*loc. cit.*, § 2 (*a*)), who find that a qualitative explanation of the spatial and temporal variations of the temperature of the lower stratosphere (*i.e.* to about 20 km.), and of the height of the tropopause, may now be given in terms of radiative processes only. Dobson gives grounds for believing that the control of temperature in the lower stratosphere is more or less equally distributed between the three gases CO_2, O_3 and H_2O, each of which probably absorbs about 5 per cent. of the upward radiation through the tropopause. He assumes that the long-wave radiation entering the stratosphere from below (about 0·3 cal. cm.$^{-2}$ min.$^{-1}$) originates, in respect of the 9·7 μ wave band absorbed by O_3, at the earth's surface (temperature about 280° K), since the troposphere is practically transparent in that band, and, in respect of wave lengths absorbed by CO_2 and H_2O, in the upper troposphere (temperature about 233° K). He then evaluates the equilibrium temperature of the lower stratosphere for each main absorption band of each gas independently, assuming the radiation from above to be negligible and obtains 200° K for CO_2, 250° K for O_3 and about 180° K for H_2O. Thus a relative increase in the amount of O_3 would raise the temperature of the stratosphere, while a relative increase of H_2O would lower the temperature. Since the mixing ratio of CO_2 to air may be taken as constant (§ 2 (*b*)) the effect of this constituent will only be felt in the general level of temperature.

Dobson then considers the nature of the variations in the tem-

perature of the lower stratosphere arising from the observed variation of O_3 in space and time. The temperature itself must be determined in part by the intensity of the upward radiation at the tropopause, *i.e.* by the temperature of the troposphere, which lags in phase behind the annual variation of solar radiation by a month or more. But the ozone content is a maximum in spring and a minimum in autumn, with greater quantities present, therefore, before the summer solstice than after. Thus the temperature wave of the lower stratosphere, where most of the ozone absorption is concentrated, will tend to be ahead of the troposphere wave. This is indeed the case, the maximum of stratosphere temperature in mid-latitudes being practically at the summer solstice. Again, the mean ozone content increases considerably with increase of latitude, accounting on Dobson's argument for the warmer stratosphere and, therefore, lower tropopause in polar regions. These effects of season and latitude suggest that a rise of 1° C. in stratosphere temperature is accounted for by an increase of 0·004 to 0·010 cm. O_3 at S.T.P. Similar considerations will account in the main for the distribution of height and temperature of the tropopause in the area of a depression of middle latitudes (cf. § 2 (*c*)). Finally, the slow and then more rapid rise of temperature with height in the stratosphere is attributed to the relative increase of O_3 with height, though in the upper levels the absorption of solar energy will partly contribute to this effect. Thus the main features of the lower stratosphere are qualitatively accounted for in terms of ozone content only. No doubt there are effects also of variation in the water-vapour content, but their elucidation will necessarily wait on further hygrometric observations. In any case, it is now clear that, on account of the smaller quantities and smaller absorption coefficients of water vapour than were earlier assumed, the temperature and other characteristics of the stratosphere are much less controlled by water vapour than was thought likely a decade ago. It also seems unlikely that dynamical effects should be the direct cause of any of the main features of the temperature distribution in the stratosphere.

The complete quantitative evaluation of the temperature of radiative equilibrium of the stratosphere and of its variations in space and time must, of course, take account of the solar absorption as well as the terrestrial radiation, but from the evidence presented in this and earlier sections the problem now appears eminently tractable. But further observations of water-vapour content, ozone distribution, a finer resolution of the water-vapour and carbon-dioxide line and band structure, and more complete information on

the effects of pressure and temperature on the absorption spectra, are required in order to obtain thoroughly reliable values. Meanwhile, we may consider that the temperature distribution up to about 50 km. is accountable for in a very qualitative fashion.

ORGANIC CHEMISTRY.

By O. L. BRADY, D.Sc., University College, London.

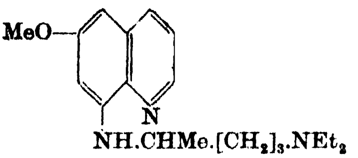
SYNTHETIC ANTIMALARIALS.—The cutting off of supplies of quinine from the East Indies greatly stimulated the search for effective substitutes for the treatment of malaria. The lifting of the ban on publication of work of national importance in this field has resulted in the appearance of reports showing the progress that has been made.

An account of one of the most important developments appears in a series of papers from the Research Laboratories at Blackley of Imperial Chemical Industries, Limited, and from the University of Manchester dealing with the investigation, started in 1942, which led to the preparation of paludrine, N^1-*p*-chlorophenyl-N^5-*iso*-propyldiguanide. (Curd and Rose, *J. Chem. Soc.*, 1946, 343, 362,729; Curd, Davis and Rose, *ibid.*, 351; Hull, Lovell, Openshaw, Payman and Todd, *ibid.*, 357; Curd, Raison and Rose, *ibid.*, 366; Curd, Davis, Owen, Rose and Tuey, *ibid.*, 370, 720; Curd, Richardson and Rose, *ibid.*, 378; Basford, Curd and Rose, *ibid.*, 713.) This drug was first tested in avian malaria by Curd, Davy and Rose in 1945 and in human malaria in the same year by Adams, Maegraith and others in Liverpool and by Fairley in Australia. Paludrine has been used successfully in the treatment of benign tertian malaria and in acute attacks of malignant tertian malaria; it has a much wider therapeutic range of activity than quinine or mepacrine and produces no serious toxic side effects (*British Medical Journal*, 1946, 903). Although the clinical picture cannot be complete until sufficient time has elapsed to ascertain whether radical cures are effected, it has been concluded that paludrine has proved superior to all known antimalarial drugs (Fairley).

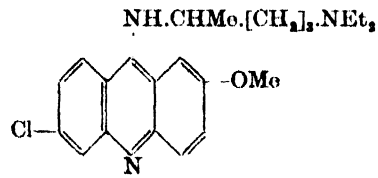
Apart from its curative and prophylactic effects, paludrine has two other advantages over mepacrine: its synthesis on the large scale is not particularly difficult and, being colourless, it does not produce an unsightly yellow staining of the skin when administered over long periods.

The discovery of paludrine was not achieved by a hit-and-miss method as is commonly, but often mistakenly, supposed to be the case in the finding of new therapeutic agents, but resulted from

ingenious reasoning. The object set themselves by the investigators was to obtain a new synthetic substitute for quinine without the disadvantages of mepacrine, namely, its liability, sometimes, to produce symptoms of intolerance, its tendency to impart a yellow colour to the skin and its complicated synthesis, which militates against its use for the mass treatment of poor communities. It was thought that the high toxicity of pamaquin [I] and mepacrine [II] were due to the presence in the former of the quinoline and in the latter of the acridine nucleus, both heterocyclic systems foreign to the animal body.



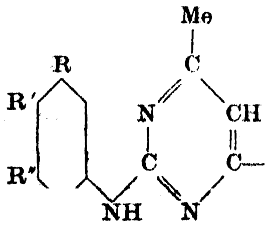
[I]
Pamaquin



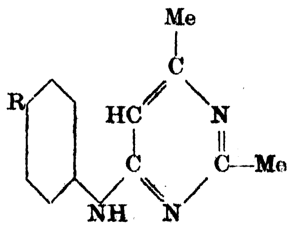
[II]
Mepacrine

If an antimalarial structure could be built up on the basis of a ring system of biological importance the animal body might possess more tolerance for such a compound, since the development of new methods of detoxification would not be called for, but only an adaptation of some process already utilised. The malaria parasites during part of their life cycle in the human host are generally believed to be intracellular, and the importance of pyrimidine derivatives in cell chemistry suggested that there might be some connection between them and the biological processes of the malaria plasmodia. It was decided therefore to investigate the use of this heterocyclic ring in building up antimalarials.

Compounds of the types [III] and [IV]



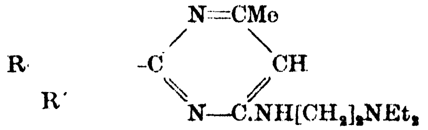
[III]



[IV]

when in [III] R = R″ = H, R′ = OMe, R = R″ = H, R′ = Cl; R = R″ = Cl, R′ = H and in [IV] R = OMe, were tried but found to be without

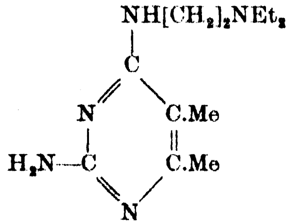
antimalarial activity. Pyrimidine derivatives [v] were then prepared, containing dialkylaminoalkylamino groups characteristic of mepacrine and pamaquin, but were still inactive.



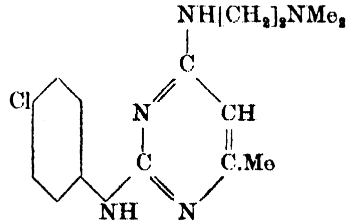
[v]

R = R′ = H ; R = OMe, R′ = H ; R = H, R′ = OMe ; R = Cl, R′ = H

On the other hand, 4-substituted-2-amino-5 : 6-dimethyl pyrimidines, *e.g.* [vi], and 2-substituted-anilino-4-aminoalkylamino-6-methyl pyrimidines, *e.g.* [vii], had antimalarial properties.

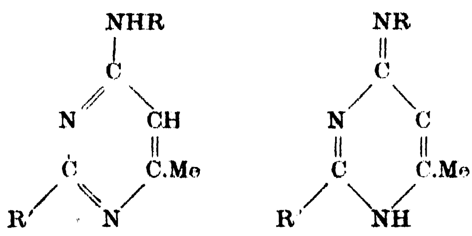


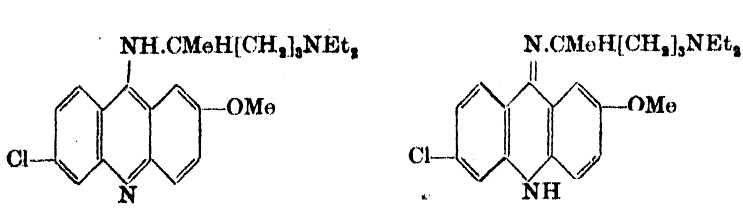
[vi]



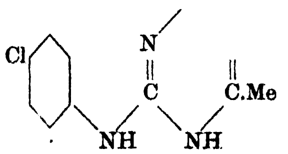
[vii]

The 4-substituted compounds were of special interest, as they were capable of an identical tautomeric change which Schönhöfer (*Z. physiol. Chem.*, 1942, **247**, 1) related to the antimalarial activity of mepacrine.

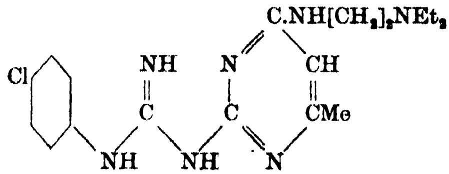




Consideration of the skeleton of the tautomeric form of [VII], that is [VIII], suggested that the 2 phenylguanidino-4-aminoalkylamino-6-methyl pyrimidines, *e.g.* [IX], might be active and this was found to be the case.

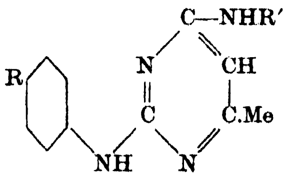


[VIII]

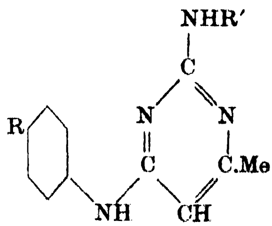


[IX]

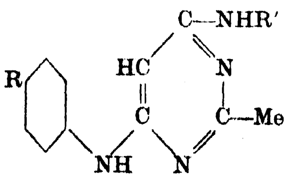
The final step resulted from a consideration of various compounds whose activity had been investigated. The isomeric pyrimidine derivatives [X] and [XI] both had antimalarial activity, but [XII] had none.



[X]

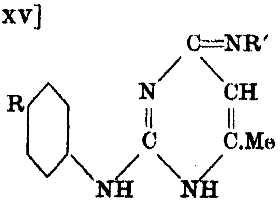


[XI]

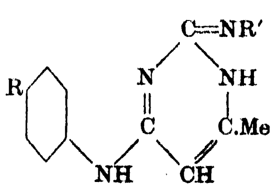


[XII]

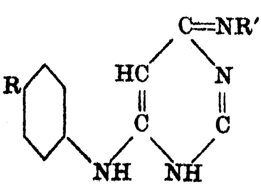
All these are capable of tautomeric change giving [XIII], [XIV] and [XV]



[XIII]

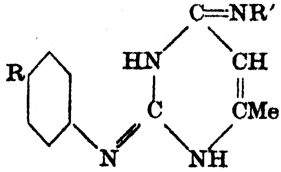


[XIV]

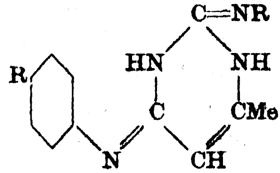


[XV]

but only the first two can undergo a second tautomeric change at the same time to [XVI] and [XVII].



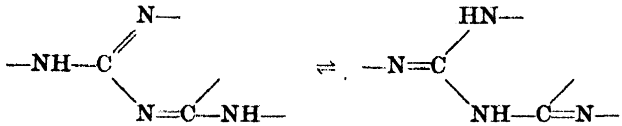
[XVI]



[XVII]

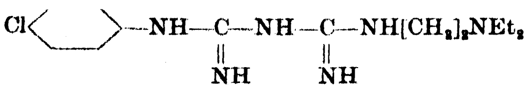
In [XV] this second change is blocked by the first.

The salient features necessary for antimalarial action seemed, therefore, to rest upon the possibility of two simultaneous tautomeric changes and to reside in the system [XVIII]

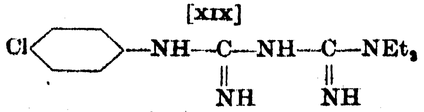


[XVIII]

and it seemed possible that a ring system was unnecessary. The diguanide molecule contained the required structural features in their simplest form. The diguanide [XIX] was prepared and surprisingly found to be inactive, and it is suggested that this might be due to the highly basic character of the molecule; on the other hand the simpler compound [XX] was markedly active.

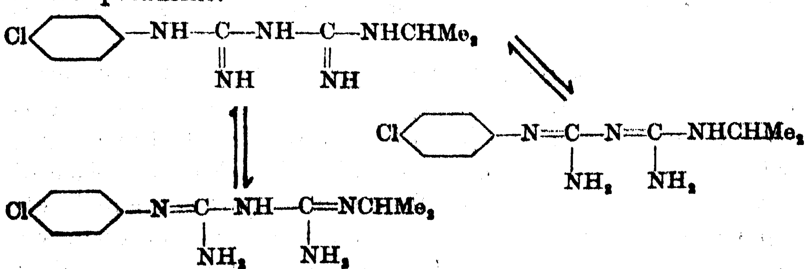


[XIX]



[XX]

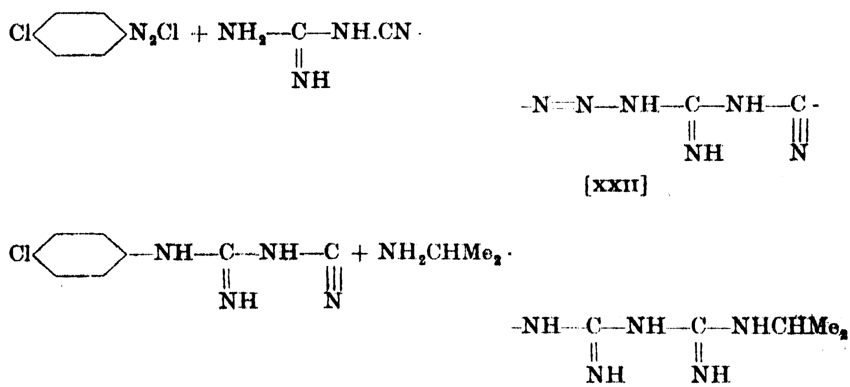
By substituting various alkyl groups for ethyl the most active product proved to be the mono*iso*propyl derivative [XXI] now named paludrine.



[XXI]

Paludrine is synthesised by condensing *p*-chlorobenzene diazonium chloride with dicyandiamide to give the triazine [xxii], which was decomposed in a mixture of β-ethoxyethanol and 10N-hydrochloric acid to give *p*-chlorophenyldicyandiamide [xxiii]. This was condensed with *iso*propylamine in the presence of copper sulphate. The paludrine was separated as a copper complex which was decomposed by sodium sulphide. The product was purified by reformation of the copper complex and precipitation of the copper again by sodium sulphide.

The base crystallises from toluene in colourless rectangular plates m.p. 129° and the hydrochloride in colourless needles from water m.p. 243–244°.



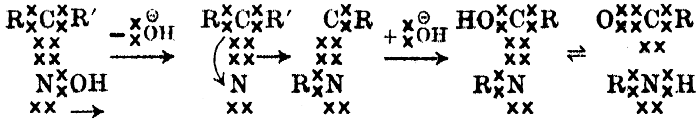
[xxii] [xxiii]

This investigation has involved the preparation and test for antimalarial activity of very many compounds resulting from small successive changes in structure; for example, in the series of which [vii] is a member, the effect of various substituents in different positions in the benzene nucleus was investigated. It was found that substitution in the para position led to higher activity than in the ortho or meta and that compounds with such substituents as Me, NO_2, OMe, etc., were active, but that the *p*-chloro-compounds were more so.

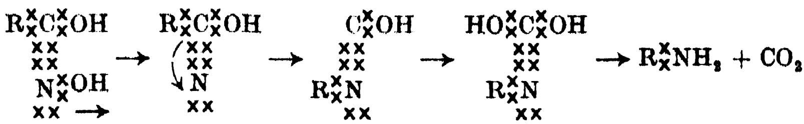
Mechanism of the Beckmann, Lossen and Curtius Changes.—These molecular rearrangements are now generally regarded as involving the elimination of a part of the molecule with the electron pair which constituted the co-valent link. This leaves a place of electron deficiency which captures from another part of the molecule a group with its electron pair. The part first eliminated then forms, in the case of the Beckmann and Lossen changes, a new co-valent

link at the point from which the migrating group has come or, in the case of the Curtius change, a molecule of nitrogen escapes.

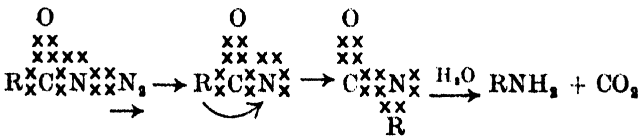
The mechanism can be pictured as follows :



Beckmann Change



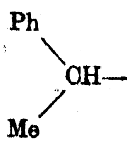
Lossen Change



Curtius Change

It is supposed that at no time during the change is the free radical $R^{\times}_{\times}$ formed, but that the nitrogen as it loses its interest in the $^{\times}_{\times}OH$ acquires an interest in the $^{\times}_{\times}R$, which does not lose completely its association with the C until it forms a complete co-valent link with N, which occurs only when the $N^{\times}_{\times}OH$ co-valency has completely broken.

Additional evidence that this is correct has been supplied by Campbell and Kenyon (*J. Chem. Soc.*, 1946, 25), who show that, where R = (+)Ph.CHMe, over 99 per cent. of the optical activity of the compound is retained after the Beckmann, Lossen and Curtius changes. Had the reaction involved the formation of the free radical



racemisation would have occurred.

PHYSICAL CHEMISTRY. By J. W. Smith, D.Sc., Ph.D., F.R.I.C., Battersea Polytechnic.

The Mechanism of Oxidation and Reduction Reactions involving Electron Transfer.—One of the simplest and yet most interesting forms of chemical change is that in which the primary reaction, at any rate, involves only electron transfer, causing the conversion of a molecule into a charged ion or vice versa. A considerable time was devoted to these reactions during a General Discussion on Oxidation held by the Faraday Society during September 1945 and reported in the *Transactions* of that Society for March and April 1946.

Reversible reactions of the electron transfer type have long been known and utilised in oxidation-reduction electrodes and in redox indicators. One of the most familiar examples is the quinol-quinone reaction, which was formerly supposed to be of the form

$$C_6H_4(OH)_2 \rightleftharpoons C_6H_4O_2'' + 2H^+ \; ; \; C_6H_4O_2'' \rightleftharpoons C_6H_4O_2 + 2\varepsilon.$$

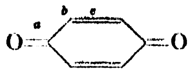
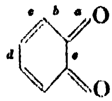
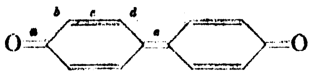
As the great majority of the compounds which are discussed here are homologues or analogues of quinol and quinone, the compounds will be written in the general form as QH_2 for the uncharged reduced form and Q for the uncharged oxidised compound. Therefore the essential reactions as given above will be written

$$QH_2 \rightleftharpoons Q'' + 2H^+ \; ; \; Q'' \rightleftharpoons Q + 2\varepsilon.$$

The quinones are an example of the general class of molecules, including also unsaturated aldehydes and ketones, which contain conjugated double-bond systems with loosely bound electrons, and which consequently can readily donate or accept electrons. Such reactions will lead to no appreciable change in the skeleton of the molecule and therefore may be expected to have low energies of activation.

One of the most fundamental theoretical aspects of the subject, which has been attacked by Coulson (*Trans. Faraday Soc.*, 1946, **42**, 106) is the question of the electron distribution in these compounds. It has been established that in this class of compounds conjugation occurs with aromatic and other unsaturated carbon groups so that the bonds involved become intermediate in character between single and double bonds. They are described by Coulson in terms of their " mobile order " p, which is zero and unity for pure single and double bonds, respectively, and has intermediate values for bonds similar to those present in benzene, for which particular case $p = 0{\cdot}67$. Utilising the method of molecular orbitals, these bond orders have been calculated for a number of simple cases, and the bond-lengths deduced from them are found to be approximately equal to the observed values when data for the latter are

available. The bond orders deduced for the various linkages in a few simple molecules are as follows :

		p_a	p_b	p_c	p_d	p_e
butadiene	$CH_2 \overset{a}{=} CH \overset{b}{—} CH \overset{c}{=} CH_2$	0·894	0·447	0·894		
acrolein	$O \overset{a}{=} CH \overset{b}{—} CH \overset{c}{=} CH_2$	0·819	0·347	0·920		
glyoxal	$O \overset{a}{=} CH \overset{b}{—} CH \overset{c}{=} O$	0·885	0·179	0·885		
quinone		0·795	0·305	0·889		
o-quinone		0·822	0·356	0·833	0·448	0·154
diphenyl-quinone		0·740	0·369	0·820	0·469	0·596

Thus it may be inferred that in glyoxal, where no system of conjugated C—C bonds occurs between the carbonyl groups, the two C=O linkages are almost the same as in the normal carbonyl group, for which $p = 0·895$, *i.e.* the bonds are much more closely " fixed " than in acrolein. On the other hand, the effect of the conjugation is much more pronounced in quinone, for which the values of p_b and p_c lead to calculated bond lengths of 1·46 and 1·35 A, respectively, as compared with the observed values of 1·50 and 1·32 A for the " single " and " double " bonds. In this case, therefore, the bonds are less " fixed " than in glyoxal, and the electron system is more mobile, an effect which is even more pronounced in the case of diphenyl quinone. Such compounds can be likened to a restricted extent to metallic conductors, where the " electron gas " can move freely, and consequently it is to be anticipated that such a system can readily act as an electron donor or acceptor in much the same way as a metal, without the charge addition or deficiency being regarded as residing exclusively at one point.

It is interesting to note the interpretation of this conception of bond order in terms of the contributions of each of the possible canonical structural forms to the ground state of the molecule. This has not been evaluated for quinone, but for the case of acrolein the proportions of the three possible structures are

$O{=}CH{—}CH{=}CH_2$ . . . . . . 0·632

$\bar{O}{—}\overset{+}{C}H{—}CH{=}CH_2$ . . . . . . 0·078

$\bar{O}{—}CH{=}CH{—}\overset{+}{C}H_2$ 0·289

Thus the form in which the charges are at opposite ends of the molecule is more important than that where the charges are adjacent, this accounting for the bond fixation in glyoxal and the successively greater electron mobilities in quinone and diphenyl quinone.

This concept of bond fixation is very important in considering the oxidation-reduction potentials of systems of the Q—QH_2 type. Branch and Calvin found an empirical relation connecting the oxidation-reduction potential with the number of ground-state canonical forms N in the oxidised and reduced forms;

$$E_o = 0{\cdot}254 + 1{\cdot}351(N_r - N_o)/(N_r + N_o).$$

Evans, on the other hand, applies Coulson's concept to the problem (*Trans. Faraday Soc.*, 1946, **42**, 113). He points out that the energy change involved in the reaction $Q + H_2 \rightarrow QH_2$ is given by

$$-D_{H_2} - 2D_{C=O} + 2D_{OH} + D_{C=C} - R_Q + R_{QH_2},$$

where D_{H_2} is the heat of dissociation of hydrogen, $D_{C=O}$ and $D_{C=C}$ are the heats of opening of the C=O bond to $\mid$C—O$\mid$ and C=C bond to —$\mid$C—$\mid$C—, respectively, D_{OH} is the heat of dissociation of —O—H, and R_Q and R_{QH_2} are the resonance energies of Q and QH_2, respectively. Evidently on passing from one quinone to another D_{H_2}, $D_{C=O}$, $D_{C=C}$, and D_{OH} are sensibly constant, whilst since the molecules Q and QH_2 differ little in mass, moments of inertia, or internal vibration frequencies the entropy change $\triangle S$ for the reaction will vary little in a series of quinones. Hence the change in free energy ($\triangle G$) of the reaction, given by $\triangle G = \triangle H - T\triangle S$, as we pass from one quinone to another is determined at constant temperature by the term $R_{QH_2} - R_Q$. The value of R_{QH_2} is taken by Evans as approximately equal to the resonance energy of the corresponding hydrocarbon, evaluated by the molecular orbital method, whereas R_Q is estimated by using the bond fixation method. The resulting values of $R_{QH_2} - R_Q$ give approximately a straight line relationship when plotted against E, the oxidation-reduction potential of the Q—QH_2 system for the series of ortho- and para-quinones, although there is some discrepancy between the two series. However, as pointed out by Evans, the ionic forms are important in determining the resonance energy and electron behaviour in a quinone, and treatments neglecting this must be considered as very approximate.

This approach, however, considers only the initial reactant and the final product, but it has long been known that intermediate compounds, often highly coloured, are produced in these reactions, *e.g.* quinhydrone in the oxidation of quinol to quinone. These were

formerly regarded as double compounds, *e.g.* $C_6H_4(OH)_2$, $C_6H_4O_2$, and called "meriquinones." This structure was doubted even by Hantzsch (*Ber.*, 1916, **49**, 571) owing to the distinctive absorption spectra of the intermediate compounds, but he could find no compound of this type suitable for molecular weight determination. Later Weitz and Meitzner (*Ber.*, 1931, **64**, 2409) found that the meriquinone compounds from dibenzyl-$\gamma\gamma'$-dipyridylium chloride and dibenzyl-$\gamma\gamma'$-dipyridylium had a molecular weight corresponding to the single molecular radical.

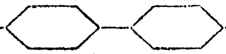
This problem was attacked by potentiometric titration methods simultaneously by Elema (*Rec. trav. chim.*, 1931, **50**, 807) and by Friedheim and Michaelis (*J. Biol. Chem.*, 1931, **91**, 355), both using pyocyanine, a methylated oxyphenazine. Both investigators observed that at low pH values a discontinuity occurred in the titration curve and concluded that the oxidation occurred through two consecutive reactions, each involving the transfer of one electron, and suggested that at pH values below about 7 a half-way reduction product of character more similar to that of a free radical than to that of a meriquinone is formed. Michaelis has called such monomeric intermediate compounds "semiquinones."

The argument developed by these investigators (*cf.* Michaelis, *Chem. Reviews*, 1935, **16**, 243) was that there are two possible series of equilibria, involving semiquinone and meriquinone ions, respectively. For the case of tetramethyl-p-phenylene diamine ($C_6H_4N_2Me_4$ = T) these can be represented

(*a*) Formation of semiquinone ion T^+	$T \rightarrow T^+ + \varepsilon$
	$T^+ \rightarrow T^{++} + \varepsilon$
	$T^{++} + T \rightarrow 2T^+$
(*b*) Formation of meriquinone ion T_2^{++}	$2T \rightarrow T_2^{++} + 2\varepsilon$
	$T_2^{++} \rightarrow 2T^{++} + 2\varepsilon$
	$T_2^{++} \rightarrow T^{++} + T$

Here T^{++} is the oxidised (quaternary ammonium salt) quinonoid ionic form. It was inferred from consideration of these relations that the formation of a semiquinone should lead to a symmetrical curve of electrode potential against per cent. oxidation of the same shape as for a one-electron system, whereas for a meriquinone it should be non-symmetrical and intermediate between the curves for the one and two electron systems. Also, the curves should be independent of the absolute concentration for a semiquinone but dependent upon it for a meriquinone. The observed potentiometric titration curves of a number of systems favoured the semiquinone view.

The first stage in oxidation processes of this type is now regarded generally as involving simple electron transfer, yielding a univalent

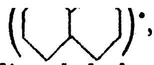
radical cation, in which, as has been seen, the electron deficiency need not be localised but is settled preferentially on the two active terminal groups. A number of examples of this type have been studied during past years by Weiss, who has summarised his conclusions (*Trans. Faraday Soc.*, 1946, **42,** 116). Such ions include those derived from quinol (HO——OH)$^{\cdot}$ and the rather analogous compounds tetramethyl-*p*-phenylene diamine (Me_2N——NMe_2)$^{\cdot}$ and benzidine (H_2N——NH_2)$^{\cdot}$, the latter having been shown to be responsible for the well-known deep blue of " benzidine blue " compounds (Weiss, *Chem. and Ind.*, 1938, 517). Relatively stable positive ions (" cationic semiquinones ") are also formed from phenazine, oxazine, and thiazine systems (Michaelis *et al.*, *J. Amer. Chem. Soc.*, 1940, **62,** 204, 1802 ; 1941, **63,** 351, 1636). As would be anticipated, these ions are all formed in acid solution, since a high hydrogen ion concentration will favour the stability of the positive ion, which in most cases tends to split off a proton thus $(QH_2)^{\cdot} \rightleftharpoons QH + H^{\cdot}$. On this account in cases where there is no mobile proton, as in the case of (Me_2N——NMe_2)$^{\cdot}$, the stability is increased. The stability will also be favoured by a low temperature and high proton affinity (*i.e.* basicity) of the free radical QH. Thus it is found that the presence in the molecule of —OH, —OMe, —NH_2, or —NMe_2 groups as substituents in the carbon ring system, or of nitrogen, oxygen, sulphur, or selenium atoms in the conjugated ring system favour the formation and stability of the ions, through decreasing their ionisation potential and increasing the proton affinity of the radical.

Similarly, anionic semiquinones, which are stable in alkaline solutions, may be formed either by the loss of a proton from the neutral radical QH or by addition of an electron to the Q molecule ;

$$QH \rightleftharpoons Q' + H^{\cdot} \; ; \quad Q + \varepsilon \rightleftharpoons Q'$$

In this case the stability of the ion is also favoured by the resonance of the negative charge.

That such ions are actually formed is also supported by the fact that the products of their dimerisation can frequently be obtained, *e.g.* from hydroquinone and 2 : 6-dibromphenol-indophenol, in solutions which are slightly alkaline, but that these dissociate giving equal amounts of the oxidised and reduced forms at lower *p*H values. Weiss has also obtained a considerable amount of evidence that the formation of such ions may also occur with hydrocarbons, *e.g.* anthracene, in concentrated acid solutions, when oxidising agents yield strongly coloured solutions (*Nature*, 1941, **147,** 512). He also

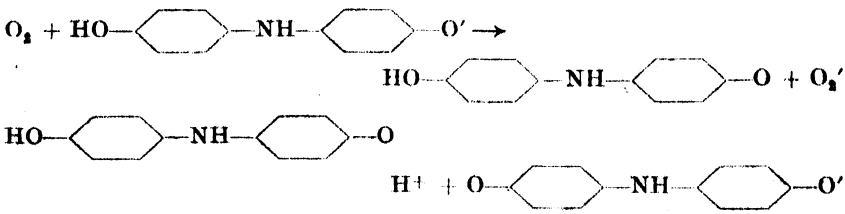
suggests that such a mechanism may also explain the formation of dinaphthyl from naphthalene by oxidation with manganese dioxide in sulphuric acid, the initial process yielding , which on loss of a proton and dimerisation gives the dinaphthyl radical and then dinaphthyl. The highly coloured compounds produced between polynuclear aromatic hydrocarbons and polynitro-compounds are also ionic in character, the coloured positive ion being formed by the transfer of an electron from the hydrocarbon to the nitro-compound (*J. Chem. Soc.*, 1942, 245). A number of highly coloured addition compounds between polycyclic compounds and bromine and iodine, which have been described by Brass and his co-workers (*Ber.*, 1932–39) are probably of the same type; the halogen is loosely bound and may be removed by treatment with thiosulphate.

Another interesting aspect of the subject has arisen through attempts to correlate the velocity of such oxidation-reduction reactions with the free energy changes associated with the primary processes involved. In 1929, La Mer and Temple studied the autoxidation of quinol, catalysed by manganous salts, in acid solution by following the oxidation-reduction potential of the solution. They found the values of the reaction velocity to be a linear function of this potential (*Proc. Nat. Acad. Sci.*, 1929, **15**, 191). This observation caused considerable interest, as it was the first time that the rate of a reaction had been found to be proportional to the free energy change involved. Since then it has been found by Chow and Kamerling that the oxygen absorption of oleic acid and linseed oil, catalysed by potassium ferricyanide, molybdicyanide, or tungsticyanide, copper-glycine, copper-pyridine, or indophenol at constant *p*H value is proportional to the oxidation-reduction potential of the catalyst (*J. Biol. Chem.*, 1934, **104**, 69; *J. Amer. Chem. Soc.*, 1934, **56**, 894), and other similar observations have been made.

Barron (*J. Biol. Chem.*, 1932, **97**, 287) studied the autoxidation by molecular oxygen of a number of reversible oxidation-reduction dyes, such as leuco-indophenol. At constant *p*H value and in the absence of catalysts there was found to be in many cases a linear relationship between the standard oxidation-reduction potential of the system and the logarithm of the time required to oxidise the dye from 2 per cent. to 50 per cent. oxidation. This implies also a linear relation between the time required for oxidation and the free energy changes ($-\Delta G$) for the reaction. Later, Dimroth (*Angew. Chem.*, 1933, **46**, 571) found a similar relationship between

the rates of reaction and the oxidation reduction potential of the system Q—QH_2 for the interaction in glacial acetic acid solution between a series of quinones (Q) and oxidisable compounds (XH_2) such as dihydrocollidine carboxylic ester and *o*-tolylphenyl semicarbazide ($XH_2 + Q \rightarrow X + QH_2$).

In a further attempt to throw light on the mechanism of such reactions, Baxendale and Lewin (*Trans. Faraday Soc.*, 1946, **42**, 126) have studied the direct oxidation by oxygen gas of the leuco compounds of phenol-, *o*-bromophenol-, and *o*-chlorophenol-indophenols. They find the velocity of oxidation to be directly proportional to the concentrations of the leuco-compound and of oxygen and inversely proportional to the hydrogen ion concentration. They deduce, therefore, that the rate-determining step in the reaction is either electron transfer from the first dissociated state of the leuco-compound, followed by proton transfer, or these two processes may occur in one step as hydrogen transfer



Further, from the velocities of the reactions at various temperatures, they deduce that the overall activation energy in each case is about 18·4 kg.-calories. Also, at the same temperature and *p*H, the velocity constants were found to be equal within experimental error for each indophenol. If it is the first dissociated state of the leuco-compound which is involved, then evidently the velocity constant under otherwise constant conditions will be proportional to its concentration in the solution. As $[QH'][H^+]/[QH_2] = K$, the dissociation constant, the velocity of reaction would be expected to be given by

$$-d[QH_2]/dt = k'[QH'][O_2] = k'K[QH_2][O_2]/[H^+]$$

Since the observed velocity constant k'' ($= k'K$) is constant for the series at constant *p*H, the true velocity constant k' is evidently inversely proportional to the dissociation constant of the reaction leading to the formation of the ion which is oxidised.

This the investigators regard as reasonable, since oxidation probably involves the removal of an electron from QH′ and hence depends on the ionisation potential of QH′. The ionisation of QH_2 to QH′ involves in electron affinity of QH, *i.e.* also the ionisation

potential of QH′, and therefore in considering the energetics of the two reactions concerned this ionisation will enter into each but with opposite signs. Therefore, if this term constitutes a large part of the free energy changes involved, it would be inferred that a change in ionisation potential would cause the observed velocity constant to vary inversely with the first dissociation constant of the reduced compound.

This reaction mechanism, however, does not accord with the straight line log k – $\triangle G$ relationship observed by Barron. Baxendale points out that the more rapid rate of oxidation found by Barron may be associated with an electrode equilibrium of the type $Q'' \rightleftharpoons Q + 2\varepsilon$ set up on the colloidal palladium used in the reduction to the leuco-compound, but it is deduced that if such were the case the slope of the curve of $\log_{10}k$ against E^o would still be $zF/2.3RT$ or about 33, whereas Barron found a slope of about 4.

An obvious corollary, which does not seem to have been pointed out, is that this same type of electron-transfer mechanism is in accord with the observed relationship between the potential of the quinone—quinol (quinhydrone) electrode and the quinone, quinol, and hydrogen ion concentrations, or more precisely, activities. This is usually expressed in text-books by supposing that the electrode equilibrium involves the doubly charged hydroquinone ion and quinone molecules, thus: $Q'' \rightleftharpoons Q + 2\varepsilon$. For such equilibria the electrode potential can be expressed in the form $E = E^o + \frac{RT}{zF}\ln\frac{a_o}{a_r}$, where a_o and a_r represent the activities of the oxidised and reduced forms, respectively, z is the number of electrons transferred in the electrode process, and E^o is the electrode potential when the activities of the two forms are equal. The dissociation of quinol is then represented as $QH_2 \rightleftharpoons Q'' + 2H^+$, the dissociation constant being written $K = a_{Q''}.a_{H^+}{}^2/a_{QH_2}$. This leads to the expression

$$E = E^o + \frac{RT}{2F}\ln\frac{a_Q}{a_{Q''}} = E^o + \frac{RT}{2F}\ln\frac{a_Q . a_{H^+}{}^2}{K . a_{QH_2}}$$

$$= E^{o\prime} + \frac{RT}{2F}\ln\frac{a_Q}{a_{QH_2}} + \frac{RT}{F}\ln a_{H^+}$$

where $E^{o\prime}$ has the significance of being the electrode potential when the activities of quinone and undissociated quinol are equal (as is approximately the case when quinhydrone is employed in this electrode under circumstances such that the concentration of undissociated quinol can be taken to represent all the reduced form present) and the hydrogen ion activity is unity.

As, however, the electrode is normally used in solutions of pH

not exceeding about 8, it is evident that this treatment is incomplete, since the concentration of the Q″ ion will be very low indeed, the predominating ion being QH′. If, however, the successive reactions are taken to be of the form;

$$QH_2 \rightleftharpoons QH' + H^+ \quad . \quad . \quad . \quad (1)$$
$$QH' \rightleftharpoons QH + \varepsilon \text{ (at electrode)} \quad . \quad . \quad . \quad (2)$$
$$QH \rightleftharpoons QH^+ + \varepsilon \text{ (at electrode)} \quad . \quad . \quad . \quad (3)$$
$$QH^+ \rightleftharpoons Q + H^+ \quad . \quad . \quad . \quad (4)$$

the dissociation constants for the reactions (1) and (4) in the solution are given by $K_1 = a_{QH'}.a_{H^+}/a_{QH_2}$ and $K_4 = a_Q.a_{H^+}/a_{QH^+}$, respectively, whilst the electrode potentials for the two electrode reactions (2) and (3) can be expressed

$$E_2 = E_2^o + \frac{RT}{F} ln \frac{a_{QH}}{a_{QH'}}; \quad E_3 = E_3^o + \frac{RT}{F} ln \frac{a_{QH^+}}{a_{QH}}.$$

But for equilibrium in the system E_2 and E_3 must be equal, *i.e.* $E_2 = E_3 = E$, and hence

$$2E \quad E_2 + E_3 = E_2^o + E_3^o + \frac{RT}{F} ln \frac{a_{QH'}}{a_{QH'}} . \frac{a_{QH^+}}{a_{QH}}$$
$$= E_2^o + E_3^o + \frac{RT}{F} ln \frac{a_Q a_{H^+}^2}{K_1 K_4 . a_{QH_2}}$$

Putting the terms which are invariant at constant temperature in the form E^o this becomes

$$E = E^o + \frac{RT}{2F} ln \frac{a_Q}{a_{QH_2}} + \frac{RT}{F} ln a_{H^+}$$

It may be added that the same relationship may also be deduced if it is assumed that the last two stages of the reaction are

$$QH \rightleftharpoons Q' + H^+, \text{ and } Q' \rightleftharpoons Q + \varepsilon.$$

Mechanisms involving the transfer of a single electron are very attractive owing to their simplicity, but in some cases it does appear that other forms of ions are involved. For instance in the autoxidation of duroquinol ($C_6(CH_3)_4(OH)_2$) to duroquinone and hydrogen peroxide, the rate of reaction was found by James and Weissberger (*J. Amer. Chem. Soc.*, 1938, **60**, 98) to be proportional to the square of the hydroxyl ion concentration, indicating that the first step is the formation of the $C_6(CH_3)_4O_2''$ ion. They consider that the evidence obtained indicates that two processes then occur: (*a*) interaction of the ion with oxygen with velocity directly proportional to the concentrations of oxygen and of the ion; and (*b*) further reaction with the duroquinone already formed, with velocity proportional to the concentrations of quinone and of the ion and independent of the oxygen concentration.

A reaction involving electron transfer as the primary process, when activated photochemically, amounts to a photo-electric effect. Such behaviour was observed by G. N. Lewis and his co-workers (*J. Amer. Chem. Soc.*, 1942, **64**, 2801 ; 1943, **65**, 2419, 1424), who irradiated tetraphenylhydrazine in rigid solvents with ultraviolet light, when the solutions became coloured and showed three main absorption bands attributable to NPh_3, NPh_3^+ and $N_2Ph_4^+$. They inferred that the light caused dissociation into the $N_2Ph_4^+$ ion and an electron, the former disappearing through two parallel mechanisms, *viz.* recapture of an electron and dissociation into NPh_2 and NPh_2^+

$$N_2Ph_4 + h\nu \longrightarrow N_2Ph_4^+ + \varepsilon \,;\quad N_2Ph_4^+ + \varepsilon \longrightarrow N_2Ph_4 \,;$$
$$N_2Ph_4^+ \longrightarrow NPh_2 + NPh_2^+$$

Lewis calls the initial product of the electron emission an " odd ion." Similar behaviour was observed on irradiation of oxazine, thiazine, and leuco-dyes in an alcohol-isopentane-ether mixture at liquid air temperature. With oxazine and thiazine, for instance, two semiquinone forms are produced, one by ejection of an electron and the other by loss of a proton from the first on standing. The process can therefore be represented $QH_2 + h\nu \longrightarrow \varepsilon + QH_2^+ \longrightarrow QH + H^+$. As pointed out by Weiss, however (*Trans. Faraday Soc.*, 1946, **42**, 133), this picture of the reaction is incomplete, since it occurs only in the presence of certain electron acceptors, such as ether and oxygen.

Weiss had previously (*Nature*, 1943, **152**, 176) emphasised the close relationship between these processes and the quenching of fluorescence of, for example, polycyclic hydrocarbons, chlorophyll, etc., by molecular oxygen, nitric oxide, and other molecules which have a suitable vacant electron level into which the " excited electron " from the absorbing molecule can be passed, thereby preventing it from returning to the ground state with the emission of fluorescence. Such reactions can be represented as involving the processes :

$$RH + h\nu \longrightarrow RH^* \qquad \text{(Absorption)}$$
$$RH^* \longrightarrow RH + h\nu' \qquad \text{(Fluorescent Emission)}$$
$$RH^* + O_2 \longrightarrow RH^+ + O_2' \qquad \text{(Quenching)}$$

In many cases the quenching reaction is completely reversible in the dark, but when oxygen is the quenching agent the result may be the formation of peroxides.

All photosensitised oxidation reactions are regarded by Weiss as involving three components, (*a*) the light-absorbing molecule (sensitiser), generally capable of exhibiting fluorescence, including such compounds as eosin, methylene blue, chlorophyll, uranyl salts,

etc.; (RH), (*b*) the oxidising agent, which may be molecular oxygen, hydrogen peroxide, or silver, ferric or other metallic ions, and (*c*) the acceptor, which is oxidised and must have reducing properties, *e.g.* iodide, ferrous, or sulphite ions, leuco-dyes, etc. (Acc). The reactions are classified into two groups, according as the fluorescence of the absorbing material is quenched by the oxidising agent or by the acceptor. This view offers a simple explanation of many observations in this field.

For instance, it had been observed by Kautsky, de Bruijn, and Baumeister (*Ber.*, 1933, **66, B,** 1588) that when trypaflavin and the leuco-base of malachite green are adsorbed separately on silica gel and brought into proximity, the leuco base undergoes oxidation in light provided that a low pressure of oxygen is present. If the two adsorbates are separated by more than a few millimetres or if the oxygen pressure lies outside a restricted range, however, oxidation does not occur. It was shown that the two compounds cannot come into direct contact and that the decomposition products of the trypaflavin do not cause the oxidation. It was therefore inferred that the oxygen molecules become activated through transference to the oxygen of the light energy absorbed by the trypaflavin, and then oxidise the leuco-base. As the energy absorbed was small they excluded the possibility of the formation of oxygen atoms or ozone, and suggested that a metastable activated oxygen molecule is produced.

Weiss, however, regards this case as an example of his first group of photosensitised oxidations, in which the fluorescence is quenched by the oxidising agent, in this case oxygen, and has suggested (*Naturwiss.*, 1935, **35,** 610; *Trans. Faraday Soc.*, 1939, **35,** 48) that the oxidation of the leuco-base may in such cases be brought about by the production of HO_2 radicals through the processes

$$\begin{aligned}&RH + h\nu \rightarrow RH^*\\&RH^* + O_2 \rightarrow RH^+ + O_2'\\&RH^+ \rightarrow R + H^+\\&H^+ + O_2' \rightarrow HO_2\end{aligned}$$

The HO_2 radical can then readily oxidise any suitable acceptor present, *e.g.* the leuco-base, being itself converted into HO_2' or H_2O_2.

In the second group of photosensitised reactions the quenching of the fluorescence of the absorbing molecule is regarded as being affected by the passage from the acceptor to the excited molecule of an electron which can fill the vacant level created by the optical excitation process. The acceptor in this case must therefore possess a loosely bound electron, and the primary quenching process can be represented $D^* + Acc \rightarrow D' + Acc^+$. The classical case of the

oxidation of iodide ion, sensitised by eosin and other dyes (Jodlbauer and Tappeiner, *Die sensibilisierende Wirkung fluoreszierender Substanzen*, Leipzig, 1907) and most photosensitised oxidations in solution are regarded as belonging to this group.

In such cases the initial process in the reaction between an excited dye molecule and the acceptor amounts to a photosensitised reduction, since subsequent reactions lead to the formation of the semiquinone and then through dismutation to the leuco-dye ; thus

$$D' + H^+ \rightleftharpoons DH$$
$$DH + D' \rightleftharpoons DH' + D \text{ and } DH' + H^+ \rightleftharpoons DH_2$$
$$\text{or} \quad 2DH \rightleftharpoons DH_2 + D$$

reactions of the same type as are met with in other forms of electron-transfer processes. Confirmation of this mechanism is provided by the observation of Holst (*Z. physikal. Chem.*, 1937, **179**, 172) that the normally established equilibrium in the system phenylhydrazine sulphonate—methylene blue is shifted by irradiation.

In the presence of an oxidising agent the leuco-dye may be reoxidised to the original dye either by thermal or photochemical reactions. The former involve electron-transfer reactions between the leuco-dye and the oxidising agent, which in the case of oxygen may be successively reduced to O_2' (or HO_2), HO_2' (or H_2O_2) and OH'. These reactions are frequently catalysed by metal ions (*cf.* Weiss, *Nature*, 1934, **133**, 648 ; *Naturwiss*, 1935, **23**, 64).

In some cases an ordinary molecule of the same species may act an acceptor, resulting in self-quenching of the fluorescence, which may result in the photochemical formation of oppositely charged ions from the same molecule, thus $A^* + A \longrightarrow A^+ + A'$ (Weiss and Weil-Malherbe, *J. Chem. Soc.*, 1944, 544). The production of such ions in the case of some hydrocarbons such as anthracene and chrysene is supported by Volmer's observation of the photo-conductivity of their solutions in solvents such as hexane.

A particularly important aspect of this theory is its application to the photosensitisation of the photolytic decomposition of the silver halide in a photographic emulsion. This may be explained either by a Group 1 mechanism, such as was favoured by Gurney and Mott (*Proc. Roy. Soc.*, 1938, **A, 164**, 151)

$$D^* + Ag^+ \longrightarrow D^+ + Ag$$
$$D^+ + Br' \longrightarrow D + Br$$

or by a Group 2 mechanism of the form

$$D^* + Br' \longrightarrow D' + Br$$
$$D' + Ag^+ \longrightarrow D + Ag$$

On the other hand, Sheppard, Lambert, and Walker (*J. Chem. Physics*, 1943, **11**, 263) consider that the evidence favours energy

transfer, rather than electron transfer, as the fundamental reaction in sensitisation. This appears to be a very interesting field for future developments.

GEOLOGY. By G. W. Tyrrell, A.R.C.Sc., D.Sc., F.R.S.E., The University, Glasgow.

Petrology—The Granitisation Controversy.—A lively controversy on the origin of the famous Rapakiwi granites was opened by H. G. Backlund with his paper "Die Umgrenzung der Svekofennides" (*Bull. Geol. Inst. Upsala*, XXVII, 1937, 219–69) and continued later in a paper entitled "The Problems of the Rapakiwi Granites" (*Journ. Geol.*, XLVI, 1938, 339–96). He shows that the typical coarse porphyritic granites with ovoids of potash-feldspar are always associated with ordinary granites having normal equigranular or porphyritic textures. In the field the Rapakiwi granites are "vicarious" (*i.e.* substitutionary) with the Jotnian Sandstones, and have a similar distribution on or near the boundaries between the Sveko-Fennian and the Gotho-Karelian orogenic belts.

Discussion of the characters of Rapakiwi granites leads to the conclusion that they have been formed mainly from Jotnian sandstones by processes akin to metasomatism (*i.e.* granitisation). The changes are ascribed to the influx of alkali-aluminates as "emanations," in quantities corresponding to, and fixed by, the porosity of the parental sandstones. A surplus of emanations, with increase of volume, gave rise to true dynamic magmas—the acid surface lavas of rheomorphic origin.

Backlund's views were at once vigorously challenged by H. von Eckermann in a paper on "The Genesis of the Rapakiwi Granites" (*Geol. För. Förh. Stockholm*, **59**, 1937, 503–24). Von Eckermann had previously shown that the igneous rocks of the Jotnian, including the Rapakiwi granites and basic irruptives, were genetically connected and formed a well-marked petrographic province. His main point in answer to Backlund's theory is that the Rapakiwi Granites are not contemporary with, or later than, the Jotnian sediments; in fact, the granites and associated rocks have weathered to form the basal arkoses of the Jotnian, and hence pre-dated them. Further, if the granitisation theory be accepted, the emanations that transformed the Jotnian sandstones must have had a highly unusual composition—a hydrous alkaline fluid very rich in F and Ti. Again, Rapakiwi Granites are known with both roof and floor consisting of Archæan rocks.

In a rejoinder Backlund ("The Rapakiwi Puzzle," *Geol. För. Förh. Stockholm*, **60**, 1938, 105–12) has an answer to most of von

Eckermann's objections. He insists that granitisation is not a special process of the Archæan, or of great depths, but is appropriate to all fold-mountain regions. The crucial problem is that of emplacement—the space-making problem—which is solved by granitisation, but not by any theory involving huge batholithic intrusions.

In his reply von Eckermann ("The Rapakiwi Facts," *ibid.* 113–15) denies that there is any special space problem in connection with the Rapakiwis. He refers to "domed Archæan roofs" which have effectively provided room for the granite masses. The space problem, if it exists, is presented far more by the voluminous basic magmas than by the associated Rapakiwi Granites and porphyries.

Another critic of extreme granitisation theories is N. H. Magnusson who, in papers entitled "Die Granitisationstheorie und deren Anwendung für Svionische Granite und Gneise Mittelschwedens" (*Geol. För. Förh. Stockholm*, **59**, 1937, 525–47), and "Die Genesis der Svionischen Granite. Zur Diskussion über die Granitisationstheorie" (*ibid.*, **60**, 1938, 285–316) strongly controverts Backlund's views in relation to the Urgranites (Svionian) of Sweden. The geological observations of twenty years on these rocks have convinced him that Backlund's theory of the origin of granites by regional metasomatism of sediments cannot be upheld. Although he himself has been compelled to assume regional metasomatic replacement of a major order to explain the Södermanland Gneiss, Magnusson is of opinion that Backlund makes an illegitimate extension of the processes admittedly operative in the formation of the Archæan gneisses to the origin of the homogeneous granites which are clearly intrusive into them.

Backlund further summarises his views and answers his critics in a paper "Zur 'Granitisationstheorie'" (*Geol. För. Förh. Stockholm*, **60**, 1938, 177–200).

One of the best recent elucidations of the subject of granitisation is the paper by M. MacGregor and G. Wilson, "On Granitization and Associated Processes" (*Geol. Mag.*, LXXVI, 1939, 193–215). Granitisation is "widely defined as the process by which solid rocks are converted to rocks of granitic character." It seems to involve two processes: "(*a*) *Metasomatism* under the influence of permeating, highly-energised fluids—emanations—ahead of advancing magma; and (*b*) *Mechanical penetration* by magma." In the first process selective metasomatic exchanges take place between the minerals of the country-rocks and the pore-fluids, leading towards a common end-product, *i.e.* a rock of granitic character. The second process follows the first without a break, or it may overlap. It produces

material of composition intermediate between that of the magma and the invaded rocks. Mechanical injection mostly takes place at higher levels; metasomatism at the lower levels where the energy-charge is still high. At the highest levels reached the magma becomes truly intrusive and effects little change on the country-rocks.

In his paper on "Formation of Igneous-looking Rocks by Metasomatism: A Critical Review and Suggested Research," F. F. Grout (*Bull. Geol. Soc. Amer.*, **52**, 1941, 1525–76) has ranged over a wide field of literature published since Sederholm gave a new impetus to the discussion of granitisation in his paper of 1913. He has performed a useful if onerous task in following and elucidating the changes of meaning in such terms as granitisation, metasomatism, contamination, etc. Further, he schedules the criteria of metasomatic replacement under no fewer than 31 headings. Grout suggests that mere reconnaissance no longer suffices as a basis for the suggestion of large-scale metasomatic replacement, and that a promising region should be selected for thorough detailed study from all angles to provide a type with which other regions may be compared.

It is impossible to do justice to Professor H. H. Read's original and penetrating work on metamorphism and igneous action, on the origin of granite and on the processes of granitisation, within the limits of a paragraph or two. Unlike many scientific works Read's papers, with their literary style and often witty character, are as entertaining to read as they are potent to convince.

In his Address on "Metamorphism and Igneous Action" (*Brit. Assoc. Adv. Sci., 1939, Pres. Address, Sect. C—Geology*, 29 pp.) he deals mainly with the origin of regionally metamorphosed rocks after an historical review of the subject. He shows in turn that stress, load, and depth, singly or in combination, are "not enough" for regional metamorphism. There is needed, in addition, penetration and replacement of the rocks by fluids mainly of magmatic origin. A preliminary discussion of granitisation is given, and the questions of feldspathisation and metamorphic zones, the latter with special reference to Barrow's pioneer work in the Scottish Highlands, are dealt with.

Read's "Meditations on Granite, Part I" (*Proc. Geol. Assoc.*, LIV, 1943, 64–85) is mainly a discussion of the definitions, nature, origin, and differentiation of granite from the historical standpoint. The concepts "magma" and "migma" are also discussed, and the part ends with a brief endorsement of Kennedy's ideas concerning plutonic and volcanic associations.

Part II of "Meditations on Granite" (*ibid.*, LV, 1944, 45–93) deals with granitisation, again in its historical aspect. The early French and the later Fenno-Scandian contributors are fully and penetratingly discussed. Then comes a shrewd and amusing account of the Backlund–von Eckermann controversy over the Rapakiwi Granites, a discussion of the origin of big feldspars at granitic contacts, and the "mobilisation" of invaded rocks. Finally, in a "return to Lyell" Read propounds the view that there are three great classes of rocks:

1. Neptunic. The sedimentary rocks.
2. Volcanic. Lavas and associated intrusions, truly igneous or magmatic. Variation by crystallisation-differentiation.
3. Plutonic. Two associated kinds; the metamorphic rocks, and the ultra-metamorphic, migmatitic, metasomatic, granitic rocks in orogenic environments. Includes the great granite masses with the gneisses and schists.

P. Niggli, on the other hand, reaches diametrically opposite conclusions to Read's and the granitisers in his memoir on "Das Problem der Granitbildung" (*Schweiz. Min. Petr. Mitt.*, XXII, 1942, 1–84). He also takes the historical standpoint and uses the historical method, but he appeals to a different set of authorities, mainly German and Swiss. As a result the magmatic theory of the origin of granite is uncompromisingly upheld. He stigmatises the views of Van Bemmelen, Backlund, Wegmann (especially Van Bemmelen) as mystical rather than scientific.

Excellent critical discussions of granitisation based mainly on the preceding papers have been given by A. Holmes, "Natural History of Granite" (*Nature*, **155**, 1945, 412–15), and R. H. Rastall, "The Granite Problem" (*Geol. Mag.*, **82**, 1945, 19–30). For a further summary of Read's views, see SCIENCE PROGRESS, **34**, 1946, 659–69.

Backlund, fortified by perusal of Read's "Meditations on Granite," returns to the subject in a paper on "The Granitization Problem" (*Geol. Mag.*, **83**, 1946, 105–17). Much of the paper deals with the development of ideas on granitisation in Fennoscandia, and particularly with the opposition to Sederholm's views. Sederholm's early description of the process (as seen by Backlund ?) is worth quoting: ". . . it is a diffuse penetration of pre-existing rocks . . . by addition of extraneous material from below, without the mother-rocks having undergone melting at any point, and with partial exsolution of surplus constituents." Backlund says of the notorious "emanations" considered necessary for granitisation: "A minor influx of Na and Si, without visible granitic affinities, associated with suitable thermodynamic conditions, seems to be all

that is necessary to start a long series of chain reactions within the geosynclinal rocks."

In recent discussions of the processes of metasomatism and granitisation the possibility of the passage of "emanations" through solid rocks and minerals, partly by penetration of the crystal lattices, has been alluded to. Two papers by R. Perrin and M. Roubault ("Les réactions à l'état solide et la géologie," *Bull. Serv. Carte géol. Algerie*, 5 ser., No. 1, 1937; and "La granite et les réactions à l'état solide," *ibid.*, No. 4, 1939) are mentioned by Backlund as of significance in granitisation theory, but the writer has not been able to consult these papers. Fortunately, however, J. A. Bugge, of Oslo, has comprehensively reviewed the whole subject in a memoir that has just come to hand ("The Geological Importance of Diffusion in the Solid State," *Avhandl. Norske Vidensk.-Akad. Oslo, I. Math. Nat. Kl.*, 1945, No. 13, 59 pp.). According to Bugge, diffusion of "ichor" or emanations through solid rocks may take place either through the tenuous intergranular fluid films, or through the crystal lattices. "The rocks are, so to speak, immersed in a molecular and ionic disperse system of particles which move through the interstices of the minerals and through the minerals themselves, altering metasomatically every part of the rocks." Large ions such as O, OH, Cl, F, etc., probably have to diffuse in the intergranular films smaller ions through the crystal lattices of most suitable size.

Bugge considers that the above processes are responsible for the following phenomena which are arranged in order of increasing distance of diffusion: (1) Exsolution processes in mixed crystals; (2) isomorphous substitution in mixed crystals; (3) formation of reaction zones between adjacent minerals (*e.g.* coronas, etc.); (4) formation of reaction zones between adjacent rocks (*e.g.* skarns, etc.); long-distance migrations with the formation of metablastic, metatectic, and palingenetic rocks (*e.g.* granitisation, large-scale metasomatism, etc.).

In his detailed survey of a small part of the great "Coast Range Batholith near Vancouver, B.C." (*Quart. Journ. Geol. Soc.*, CI, 1945, 37–88), T. C. Phemister has produced a kind of test case to aid in the assessment of the rival claims of "magmatists" and "emanationists" concerning the origin of granite masses. The Coast Range Batholith is 1250 miles long by 125 miles across. The area studied by Phemister is 10 by 20 miles in area, situated within the contact region of the batholith. The normal rock is a homogeneous granodiorite with a more sodic leucocratic phase in the marginal zone. Further, a dioritic phase occurs to the west, which is regarded, at

least partly, as of hybrid origin. The country-rocks are metabasalts with some more acid types, which have suffered regional metamorphism at a period long antedating the emplacement of the batholith.

While admitting hybridism in the contact region described, Phemister is reluctant to extend the replacement or granitisation conception to the main mass of the batholith, and thus extrapolate from exceptional marginal conditions the view that replacement is responsible for the whole of this enormous mass. The paper was followed by an illuminating discussion in which both sides of the granitisation controversy were represented.

On the other hand, thorough-going granitisation is advocated by Miss D. L. Reynolds in her paper on " The South-western End of the Newry Igneous Complex " (*Quart. Journ. Geol. Soc.*, XCIX, 1944, 205–46). The mass is shown to be composed of hornblende-, biotite-, and porphyritic-granodiorite. Biotite-granite is regarded as having been developed from biotite-hornfels by the incoming of Na, Ca, and Si, with the concomitant removal of Al, Fe, Mg, Na, K, H, Ti, P, and Mn. The outgoing elements were fixed in adjacent belts of biotite- and diopside-hornfels, the latter being progressively basified and finally converted into pseudo-diori es. It is suggested that the basic material which migrated from the region of granitisation as a whole was fixed (*a*) in the biotite-enriched contact aureole, and (*b*) in basic and ultrabasic roof-rocks such as those which are known to cap the granodiorite elsewhere. Thus the basic and ultrabasic types which are developed are complementary to the granodiorites, and the metasomatic processes finally culminate in magma formation and intrusion.

B. C. King, in describing " The Cnoc nan Cuilean Area of the Ben Loyal Igneous Complex " (*Quart. Journ. Geol. Soc.*, XCVIII, 1943, 147–86), states that the two main syenitic masses of this complex have the form of cones with their apices pointing downward. The Cnoc nan Cuilean mass consists of pulaskite with a marginal zone of variable syenites. It is intruded into Moine Granulites which have been metasomatically altered with the introduction of albite, aegirine-augite and hornblende. The contacts of the peripheral variable syenites with the Moines are often transitional. The basic syenites are considered to be the result of hybridisation of basic metasomatised rocks by a feldspathic syenite of rheomorphic origin.

" The Garabal Hill–Glen Fyne Igneous Complex," described by S. R. Nockolds (*Quart. Journ. Geol. Soc.*, XCVI, 1941, 451–511), is 12½ sq. miles in area and is situated west of the head of Loch

Lomond. It consists mainly of a porphyritic granodiorite, but this is the final term (except aplites and pegmatites) of a series of intrusions ranging from peridotites and pyroxenites (earliest), through gabbros, pyroxene-mica-diorites, appinites, xenolithic diorites, quartz-diorites, medium granodiorites, to the porphyritic granodiorites aforesaid, named in probable order of intrusion. It is concluded that crystallisation-differentiation is the only process competent to account for the origin of this series except that, for certain types, contamination with the surrounding schists must be postulated.

"The Portencorkrie Complex of Wigtownshire," described by N. Holgate (*Geol. Mag.*, LXXX, 1943, 171–95), consists of dioritic rocks intruded by a central granite (adamellite) which has extensively hybridised the adjacent diorites at its contacts. The diorite is a hypersthene-bearing pyroxene-mica-diorite at its contact with the Silurian sediments, and passes inwards to successively more acid types originating, the author thinks, by crystallisation-differentiation. The basic diorite at the northern margin of the mass has a chilled porphyritic facies which, when not modified by the assimilation of sediments, represents the original dioritic magma. Resemblances to the Garabal Hill–Glen Fyne and other Caledonian igneous complexes are noted.

"A Hornblendic Complex, including Appinitic Types, in the Migmatite Area of North Sutherland" is described by Y. Cheng (*Proc. Geol. Assoc.*, LIII, 1942, 67–85). The main types are pyroxenites, hornblendites, hornblende-pyroxene-biotite-schists, coarse appinites and their late migmatitic derivatives, pseudo-dioritic gneisses, hornblende-augen-gneisses and granite-gneisses. The complex thus includes rocks resembling the Ach'uaine Hybrids of Sutherland and the Appinite Suite of the South-western Highlands. The parental rocks of the Complex were the results of hybridisation completed before the general migmatisation of the region, and they, in turn, were profoundly modified by the processes of that period.

The same author has dealt with "The Migmatite Area around Bettyhill, Sutherland" (*Quart. Journ. Geol. Soc.*, XCIX, 1944, 107–54), and gives the following concise summary of his work: "The migmatization of pelitic, semi-pelitic, siliceous and hornblendic rocks of the Moine Series is a record . . . of metasomatic changes brought about by the activity of alkaline solutions. Pelitic gneisses are converted by soda-metasomatism into permeation-gneisses. Semi-pelitic granulites give rise to augen-migmatites through the action of potash-bearing fluids. . . . Various types of granite-gneisses arise from the different sedimentary parents. Many

sheets of pegmatite, granite and aplite are shown by their field relations to have been formed by the gradual metasomatism of the country rocks, probably by the long-continued passage of fluids along certain channels."

G. E. Goodspee has described "Small Granodioritic Blocks formed by Additive Metamorphism" (*Journ. Geol.*, XLV, 1937, 741–62). The occurrence is a cataclastic hornfels which carries small, fresh and unsheared blocks of granodiorite often with sharp outlines, but sometimes with gradational contacts. Some of the blocks contain inclusions of the hornfels, and from some of them apophyses extend into the adjacent rock. These blocks cannot be adequately explained by cataclasis or by magmatic injection. The field and microscope evidence points to the conclusion that the blocks are the result of replacement of highly crushed parts of the hornfels by hydrothermal solutions.

In a paper on "The Metasomatism of Karroo Sediments by Dolerite," F. Walker and A. Poldervaart (*Trans. Roy. Soc. S. Afr.*, XXIX, 1942, 285–307) show that the Karroo dolerite magma is capable of converting argillaceous siltstones into a distinctive type of granophyre characterised by conspicuous prisms of pyroxene. This transformation is accomplished by metasomatic processes involving a small magmatic addition to the siltstones, mainly of cafemic oxides. Rheomorphic phenomena show that the granophyre became fully mobilised.

In a valuable paper F. F. Grout critically discusses the criteria used in determining the origin of inclusions in igneous rocks (*Bull. Geol. Soc. Amer.*, **48**, 1937, 1521–72). Segregation in place can only be suggested for glomeroporphyries and possibly orbicules. As inclusions react with the magma in which they are immersed they may be completely changed in texture and in chemical and mineral composition. The criteria of origin may thus be lost.

Sederholm described the oligoclase-rich diorites which form the great majority of orbicular "granites" as *esboïte*. P. Eskola thus writes on "The Esboitic Crystallisation of Orbicular Rocks" (*Journ. Geol.*, XLVI, 1938, 448–85) in a valuable discussion of the origin of the orbicular structure. The novelty of Eskola's theory is that the orbicules are believed to have been formed at a late stage of magmatic consolidation "when the diorite was a mush of crystals and magma."' The concretionary crystallisation is thus thought to be due to a metasomatic replacement of pre-existing minerals. The orbicular rocks of Finland in particular have such a close connection with migmatites that a genetic relation must be suspected. "When the approaching migmatite front had opened the doors

for free diffusion, one of the early effects of this may have been to start esboitic crystallisation wherever favourable materials and structures existed."

In a discussion of the occurrence of "Andalusite and Sillimanite in Uncontaminated Igneous Rocks," E. S. Hills (*Geol. Mag.*, LXXV, 1938, 296–304) expresses scepticism of the orthodox view that these minerals are always to be ascribed to contamination of magmas by highly aluminous sediments or metamorphic rocks. The occurrence of andalusite in pegmatites, etc., seems to show that aluminium silicate minerals may crystallise directly from normal granitic differentiates.

PEDOLOGY. By Professor G. W. Robinson, M.A., Sc.D., University College of North Wales, Bangor.

In an editorial article (*Soils and Fertilizers*, 1940, **3**, 147–8) the subject of pedology was commemorated in the form of an Obituary Notice. The subject attained its zenith in the thirties of the present century and seemed established as an independent science. Then a reaction set in: during the sterner times of the last war and its preparatory years, the utilitarian motive became dominant and interest in the soil as soil waned. Whilst not concurring entirely in the pessimistic views of the writer of the article, it must be admitted that the war years have not been very fruitful in advances, so far as can be judged by the available literature. Nevertheless, much useful work has been done which, without opening up new horizons, has added materially to factual knowledge. Considerable additions have been made to our knowledge of soil geography, particularly in non-European countries, and, whilst no very revolutionary changes are needed in our ideas of soil classification, the time is now ripe for a more comprehensive and detailed system.

Cryopedology.—The use of the term pedology for the study of soils as a branch of natural science has not received general acceptance and many have preferred the slightly disreputable term "soil science." A distinguished American geologist, Kirk Bryan, now proposes the term *cryopedology* for the study of the phenomena associated with the action of frost on soils and subsoils (*Amer. J. Sci.*, 1946, **244**, 622–42). During recent years these phenomena have received considerable attention from geologists and have become of immediate practical importance in connection with constructional work in northern latitudes. As affecting periglacial and glacial geology, they are also of importance for pedologists. A number of new terms are proposed, many of which will meet with opposition from those who boggle at words unintelligible to the

practical man. Yet there is an obvious advantage in having special words or terms to express conceptions in frequent use. A " coined " word can be given more precise meaning than a word or phrase whose meaning is blurred by common use. There would thus appear to be some justification for the use of such terms as *congeliturbation* for frost-action, including frost-heaving, sludging, and solifluction. The vocabulary proposed by Bryan would appear to have at least as much to recommend it as that already in use in the study of dynamical geology.

WEATHERING.—The study of weathering might belong more appropriately to the parent subject of geology but is so vital to an understanding of pedogenesis that it has received considerable attention from pedologists. R. P. Humbert and C. E. Marshall (*Missouri Res. Bull.*, No. 359, 1943, 1–60) have studied in detail the weathering of a granite and a diabase, respectively, under Missourian conditions. By the use of the electron microscope, they were able to identify the clay fraction from the weathering of granite as essentially beidellite with varying proportions of micaceous minerals and a minor complement of quartz and ferromagnesians. For diabase the picture is similar, which may reflect the dominant effect of the warm-temperate and humid climatic conditions. The authors regard the weathering of silicate minerals as beginning with an interposition of H_2O-dipoles between silicate anions and their associated cations. The extent of this reaction is governed by the solid geometry of the original structures, which affects the ease of access of the water molecules. The extent to which structure and stability are affected in this stage will vary, but in the felspars it is probably slight. In the next stage, the modified structure can now react with mobile cations in leaching waters and the predominant change will be the replacement of the active cations by hydrogen-ions. These, according to E. R. Graham (*Soil Sci.*, 1940, **49**, 277–81) may actually originate from previously formed acid clays. The ultimate result of these changes is the breakdown of the original lattice and the formation of secondary clay minerals, such as kaolinite and beidellite.

A problem that constantly confronts the pedologist in the field is that of the correspondence of the horizons of a soil profile with the underlying material. Using the conventional A, B, C nomenclature, can it be assumed that A and B, the horizons of the solum, have been developed from material represented by the underlying C ? Frequently, as for example, where sandy over-washes are present, this is clearly not so, but there are many profiles where, although A and B apparently correspond with C, proof of this is desirable.

C. H. Edelman (*Meded. LandbHoogesch. Wageningen*, 1936, **40**, 3–15) was probably the first to use heavy mineral assemblages as tests of the uniformity of soil profiles. This line of attack has been further developed by C. E. Marshall (*Missouri Res. Bull.*, No. 387, 1945, 1–75). Using zircon as an assumed immobile indicator, he calculated the gains and losses in different horizons of a profile during its development. As might be expected, losses were shown in the A and gains in the B horizons. An interesting discovery was that the sand fraction, 0·125–0·046 mm., was apparently immobile, and if this should be confirmed, it would suggest a very convenient starting-point for profile studies.

Soil-forming Factors.—In any valid system of soil classification, the characters of the individual classes should be susceptible of numerical expression. H. Jenny has done much pioneer work in attempting to derive quantitative relationships between soil properties and soil-forming factors, and his book *Factors of Soil Formation* (McGraw-Hill, 1941) marks an important stage in the development of this branch of pedology. More recently, this author has discussed the arrangement of soil series and types according to the functions of soil-forming factors (*Soil Sci.*, 1946, **61**, 375–91). He starts from the general equation:

$$s = f(cl,\ o,\ r,\ p,\ t,\ .\ .\ .)$$

where s is any soil property, *e.g.* colour, clay content, etc., cl = climate, o = bio-sequence (vegetation), r = topography, p = parent material, and t = age, and derives a number of subsidiary equations, *e.g.* :— $s = f(t)cl, o, r, p, \ldots$ which is the equation for the time function when other factors are assumed constant. Within a single area the variation of a soil property from s_a to s_b can be set out as:

$$s_b - s_a = \int_c^d \left(\frac{\partial s}{\partial F_1}\right) dF_1 + \int_e^f \left(\frac{\partial s}{\partial F_2}\right) dF_2 + \ .\ .\ .\ \text{etc.}$$

where factor F_1 varies from c to d, F_2 from e to f, and so on. Then if the definite integrals of the factors F_2, F_3, etc., are small in comparison with the definite integral of F_1, we may say that $s_b - s_a$ is mainly conditioned by F_1. A number of equations for properties s_1, s_2, s_3, etc., may be obtained and all these properties may be regarded as an ensemble which may be designated $E(s) = f(cl,\ o,\ r,\ p,\ t,\ .\ .\ .)$. Examples are given of time sequences, *e.g.* the Californian soil series, Hanford, Greenfield, Ramona, and Placentia, representing increasing maturity. Similarly, examples of litho-climatic, and topographical sequences are given. An series may represent a stage in a number of different

sequences, each of equal rank. The fact that accurate numerical values cannot be assigned to all the soil characters and related pedogenic factors does not invalidate Jenny's arguments, but it may be objected that the expression of pedogenesis in such mathematical form gives the impression of an exactitude that does not exist, or if it does exist, cannot be tested.

Another instance of the mathematical approach to the study of the organic matter balance in the soil by S. Hénin and M. Dupuis (*Ann. Agronom.*, 1945, **15** (N.S.), 17–29). According to these authors the variation in organic matter content, y, in a soil during time t is given by:

$$dy = (K_1\omega - K_2y)dt$$

where ω is the annual addition of organic matter expressed as a percentage, K_1 the isohumic coefficient of the added material, and K_2 the coefficient of destruction. The isohumic coefficient is defined as the ratio of the increase of soil organic matter to the amount added of any given material. When a state of equilibrium is reached $K_1\omega = K_2y$ and $y = \frac{K_1}{K_2}\omega$. Given an initial organic matter of Y, and supposing that there are no additions, the organic matter content y after time t is given by the equation $\frac{Y - y}{Y} = K_2t$. Under the conditions of northern France and southern England, existing experimental data yield a mean value for K_1 of 0·36, but the variations are considerable with different materials. K_2 is shown to approximate to 0·02, from data at Versailles, but the mean value from English data approximates to 0·015. It would appear, therefore, that K_1 and K_2 vary markedly with soil and site and also with the type of organic matter added.

PODSOLS.—Among the major soil groups, the podsols have probably received by far the most attention from pedologists. Many explanations of podsolisation have been given and it is commonly supposed that the process is associated with extreme acidity in the profile. The actual mobilisation and translocation of sesquioxides has been generally attributed to the action of humic and other acids capable of forming complex ferriferous ions. Although the rôle of anions has been recognised, a relatively high hydrogen-ion concentration corresponding with a soil pH of about 4·5 or less has been regarded as a necessary condition.

P. H. Gallagher (*Proc. Roy. Irish Academy*, 1942, **48B**, 213–29) assigns a subsidiary rôle to humic acids in podsolisation and considers that the process is more probably associated with simple organic anions, such as oxalic acid, liberated during the decomposition of

organic matter under certain conditions. Such a process may occur under relatively neutral conditions, since the effective agent is the organic anion, and not the hydrogen-ion. This somewhat revolutionary view of podsolisation is supported by a description by P. H. Gallagher and T. Walsh (*ibid.*, **47B**, 205–40) of certain Irish profiles, developed in calcareous drift, which present all the morphological features of podsols but which show alkaline reactions to the surface. The authors reject the possibility that the high lime status is due to added calcareous dressings.

It is possible that the alkaline Irish podsols may have some affinities with certain soils of Western Canada occurring under mixed deciduous and coniferous tree cover. These soils, which have always presented a problem in classification, resemble podsols in morphology, are developed in calcareous drifts, and show alkaline or neutral reactions throughout the profile. These soils were discussed by H. C. Moss (*Sci. Agric.*, 1937, **18**, 708–18) and earlier by A. Leahey (*ibid.*, 1932, **13**, 7–13). Whilst the latter author considered that the presence of carbonate in the profile should not exclude them from the podsols, Moss preferred to assign them to a separate group.

H. M. Galloway (*Soil Sci.*, 1940, **49**, 259–302) reports an alkaline raw-humus in the Wisconsin podsol belt associated with coniferous forest, but as it lies directly over fragmented limestone, no podsol profile is developed.

Clay-humus Complex.—Whilst for many purposes it is convenient to think of the soil as composed of inorganic and organic constituents, it is probable that the association between clay and humus is of a quasi-chemical character. L. Meyer (*Forschungsdienst*, 1941, **11**, 344–55) has actually prepared from artificial permutites and humic acids complexes similar to those occurring in tshernosems. According to Meyer, the organic component is an integral part of the structure and not merely superficially absorbed. Meyer was not equally successful with clay minerals, but concludes that such complexes arise in nature by formation *in statu nascendi* simultaneously with the formation of humus from the alteration of plant residues and of the clay minerals by weathering of primary minerals. The study of this process may have a bearing on the persistence of humus in the soil, for humus combined with clay minerals may be less subject to biological oxidation than humus not so combined. L. E. Ensminger and J. E. Gieseking (*Soil Sci.*, 1942, **53**, 205–9) found that absorption of albumen and haemoglobin retarded enzymatic proteolysis.

F. Y. Geltser (*Pedology*, 1941, No. 4, 52–61) considers humic acid

to be formed by distinct microbial syntheses, rather than by the alteration of lignins. In tshernosems and ordinary agricultural soils this synthesis is bacterial, whilst in podsols it is the result of fungal activities. On the other hand, I. D. Sedletsky and G. M. Shimakova (*C. R. Acad. Sci.* (*U.S.S.R.*), 1942, **35**, 255–7) consider the humic acids of ordinary soils and peats, respectively, to be of identical structure.

BOTANY. By Professor W. H. Pearsall, D.Sc., F.R.S., University College, London.

Ecology.—One of the more interesting recent developments in plant ecology has been the analysis of some East African vegetation types, which has demonstrated the importance of human activity in controlling the vegetation of hillsides in Uganda. The work is described by A. S. Thomas (*Jour. Ecol.*, **33**, 153). The demonstration also includes interesting inter-relations between types of land utilisation as well as the natural vegetation and the edaphic characteristics of the area studied.

The establishment of exotic species in semi-natural surroundings is recorded by E. W. Jones (*Jour. Ecol.*, **33**, 44) for regeneration of Douglas Fir (*Pseudotsuga taxifolia*) in the New Forest, where its success seems to be largely determined by the presence of a carpet of coniferous litter on the soil, the litter from deciduous trees proving to be very unsuitable. The Douglas Fir is shade tolerant in youth and seems to have distinct possibilities as a British forest tree on account of its high growth rate, but it is evident that it can only become established in Britain under somewhat specialised conditions of soil and of fruit production.

A somewhat similar subject has been discussed by A. L. Poole (*Jour. Linn. Soc.*, **53**, 63), dealing with *Phormium tenax* swamps found in certain parts of New Zealand. Although the *Phormium* in this case is a native plant, its success as a dominant in New Zealand seems to have been induced by drainage and modification of existing swamps in which the native dominant is *Typha angustifolia*.

A valuable study of the distribution and status of *Glyceria maxima* in Britain has been made by Miss J. M. Lambert (*Jour. Ecol.*, **33**, 230), in the Norfolk Broads particularly, showing that *Glyceria* establishes itself as a floating reed-swamp in comparatively calm waters and is to some extent dependent upon circulation of water and the supply of mineral salts and silt, so that it fails to maintain itself in closed systems which are entirely peaty.

Another more specialised account of marsh ecology has been contributed by R. W. Jessup (*Trans. Roy. Soc. S. Australia*, **70**, 3)

in a paper dealing with the initially saline areas adjacent to lakes Alexandrina and Albert.

G. H. Lockett (*Jour. Ecol.*, **33**, 222) has studied the availability to plants of water in chalk, and his work reveals that water is available to plants up to a suction pressure of about one atmosphere. There is a large amount of water available at higher suction pressures which may well keep alive those plants which are able to exploit it, although they cannot flourish on it or increase vegetatively to any marked extent.

A paper by J. W. G. Lund (*New Phyt.*, **44**, 196, and **45**, 56) is a study of the ecology, size and taxonomy of British soil diatoms. The diatoms described have a good general correlation with the base-deficiency and *p*H of the soils. Two species, *Caloneis fasciata* and *Pinnularia silvatica*, are confined to especially acid soils, though some species have a much wider distribution. The accurate study of these diatoms has, however, necessitated complete revision of their taxonomy with particular reference to the problems of size variation, but for details of these reference must be made to the original paper.

TAXONOMY.—In the *Jour. Linn. Soc.*, **53**, 91, M. Càrdenas and J. G. Hawkes describe a number of new and little-known species of wild potato, which were brought from Bolivia and Peru by Dr. Càrdenas and grown at the Imperial Bureaux Potato Research Station, Cambridge. Some twelve new species and combinations are described, which brings up the list of wild species of potato to the neighbourhood of 170. In the same journal there is an account of types of variation in the smooth-leaved elm, *Ulmus carpinifolia*, which includes an interesting typification of the variation of leaf form. This is contributed by R. Melville.

Under the auspices of the *Biological Flora* there has appeared the check list of British vascular plants, which has been prepared for the British Ecological Society by Professor A. R. Clapham, assisted by various specialists. The list has, as appendices, a list of the British species of *Rubus*, supplied by William Watson, and one of the British species of *Hieracium* prepared from H. W. Pugsley's forthcoming monograph. It is to be hoped that this list will produce, for a time at least, some standardisation of nomenclature in dealing with plant names. To the *Biological Flora of the British Isles* have been added new parts dealing with *Polygonum*, *P. persicaria*, *P. lapathifolium*, *P. petecticale* and *Gentiana pneumonanthe*; all of these are contributed by N. W. Simmonds.

An account of some noteworthy sedges from the Inner and Outer Hebrides has been published by J. W. Heslop Harrison (*Trans.*

Bot. Soc. Edinb., **34**, 270), which includes two species, new to the British Isles, *Carex glacialis* and *Carex brunnea*, the latter probably a recent importation. A paper by H. B. S. Womersley (*Trans. Roy. Soc. S. Australia*, **70**, 127) deals with marine algæ belonging to the *Myxophyceæ* which have been recorded from South Australia. These include a new species of *Rivularia* and a new species of the red algæ *Dasyopsis*.

An interesting feature of a recent study of the moss flora of the Hebrides by W. A. Clark and R. B. Cooke (*Trans. Bot. Soc. Edinb.*, **34**, 252) has been the discovery of *Myurium hebridarum* at comparatively high altitudes on the mountains of Rhum and South Uist, in association with arctic-alpine plants. *Myurium* has previously been reported only from near the coast. The present discoveries are held to suggest the possibility that this species might be a survivor, since it occurs on what were probably unglaciated areas.

General.—Interest in developmental research continues to grow. There have been a number of studies of growing-point development, of which one of the more generally interesting has been the examination of the long and short shoots of *Gingko biloba* by J. E. Gunckel and R. H. Whitmore (*Amer. J. Bot.* **33**, 285). The examination of the meristems of these shoots has shown that the actual meristematic apices are very closely similar and that the pattern of development is not altered, although the quantitative expressions of this development vary markedly. Most noteworthy is the much greater duration of meristematic activity in the long shoots, particularly in the region of the rippen meristem. A somewhat different mode of attack has been pursued by C. W. Wardlaw in continuing his studies of Pteridophytes (*Ann. Bot.*, *N.S.*, **10**, 97, 117). The particular point now demonstrated is that the internal morphology of the shoot depends to a large extent upon the leaf development, so that if a very young leaf primordium is destroyed or suppressed the shoot stele may develop without leaf gaps. This has now been demonstrated for *Osmunda* and *Todea*, in addition to *Dryopteris* described in a former publication. This result throws doubt on the supposition that the shoot is partly of foliar origin. In a second paper on the Onocleoid ferns, *Matteuccia struthiopteris* and *Onoclea sensibilis*, the effect of cutting away young buds has been studied, the result being that it has been shown that regeneration of meristems may take place from the cortical parenchyma, a result not hitherto recorded for ferns. The organisation of a complete apical meristem seems to be the necessary precursor of subsequent leaf development.

A paper by C. Clarence Sterling (*Amer. J. Bot.*, **33**, 35) deals with the development of the vascular tissues in *Sequoia sempervirens*.

Of somewhat wider general interest has been the application of tissue culture to problems of development in apical meristems. E. Ball (*Am. J. Bot.*, **33**, 301) has studied the growth of stem tips and the adjacent regions in two plants, *Tropaeolum majus* and *Lupinus albus*, which have very different meristematic properties. The stem organisation maintains itself in pure culture even if comparatively small fragments are used, so that the author accepts the view that the stem meristem controls its own development, and rejects the assumption that its organisation is superimposed on it as the result of external and internal conditions acting on a plastic growing tissue.

T. M. Harris (*Phil. Trans. Roy. Soc.*, **B 231**, 175) has described a number of cones of extinct Cycadales from the Jurassic rocks of Yorkshire. Evidence is brought forward as to the structure and morphology of the fruits known as *Beania* and the sporophylls of *Androstrobus*. Both of these are associated with the leaf *Nilssonia*, and evidently all belong to the same plant, and there is overwhelming evidence that this should be included among the Cycads. It would appear that it is a Cycad closely related to existing *Zamioideae*. Professor Harris has also published a revision of *Williamsoniella* and has re-described the floral organs from new material in the British Museum. Another important paper is the description of the lower Devonian flora from the Senni Beds of Monmouthshire and Breconshire by W. M. Croft and W. H. Lang (*Phil. Trans. Roy. Soc.*, **B 231**, 131). Hitherto undescribed, fructifications have been found in organic connection with the remains of vegetative shoots of *Psilophyton princeps*. This fructification is quite unlike *Dawsonites*, which also occurs among the material. Other plants include species of *Gosslingia*, *Zosterophyllum*, and *Cooksonia*, while *Sporogonites*, *Sciadophyton* and *Taeniocrada* are recorded for the first time for the British Isles. One of the striking features of the material is, however, the presence in these rocks, along with large and definite terrestrial vascular plants, of the peculiarly organised Nematophytales (*Prototaxites*, *Nematothallus*). This association gives additional support for the supposition that the Nematophytales should be regarded as land plants.

ZOOLOGY. By William Holmes, M.A., D.Phil., The University, Oxford.

The Biology of the Individual.—The biologist is often content to assume that all animals of the same species are identical: one rabbit is as good as another for many practical purposes. Nevertheless, it is a consequence of the particulate mechanism of inheritance that each animal may have received from its parents any

one of a virtually infinite variety of possible combinations of endowments. The unit factors—the genes—by which the characters of an individual are determined are so numerous that it is theoretically possible that every animal is unique in its inheritance. And it is not only theoretically possible, for in natural populations of those species that have been genetically analysed it has been shown that all individuals are in fact unique (see E. Mayr, *Systematics and the Origin of Species*, New York, Columbia, 1944). To this generalisation there are, of course, exceptions: the members of highly inbred strains—the "pure lines" of genetic experiment—approach closely to the identity of inheritance that is found to perfection in uniovular twins; it may also be seen amongst individuals formed by asexual reproduction, such as the clones of *Paramecium*, when the genetic material is handed on unmodified from the single parent to its many offspring.

An animal normally develops from a single cell, and within this cell its hereditary endowment is to be found as a relatively small amount of living material. This material is in some way ordered, and in its unique structure and organisation lies the uniqueness of the in ividual, for it initiates and determines all the complex series of events that lead to the establishment of the final form of the adult. Most of the hereditary material becomes "visible" at cell division confined within the chromosomes, and the investigation of the structure of these bodies is therefore a matter of great interest. Fundamental analysis can only be con ucted by the methods of physics and chemistry, refined and specialised as is necessary for the study of the complex molecular systems characteristic of the structural basis of life. Recent advances in the investigation of the structure of the chromosomes are discussed in the *Cold Spring Harbor Symposium*, 1941, **9**, by Darlington (*Nature*, 1942, **149**, 66) and Caspersson (*Nature*, 1944, **153**, 499): considerable progress has been made, for example, by the study of the distribution of the selectively ultra-violet absorbing amino-acids.

The study of the elaborate causal sequence set in progress by the hereditary determinants—the genes—is the subject matter of experimental embryology. Much of this analysis has reached a chemical level, as was witnessed by the publication during the war of Needham's *Biochemistry and Morphogenesis* and Brachet's *Embryologie Chimique*, but as yet relatively little connection has been made between the genetic and adult uniqueness with which we are here concerned.

Our human conviction that each of us is somehow different from everyone else receives most striking confirmation from the fact that

the skin of one human being cannot successfully be grafted on to the body of another, unless the donor and recipient are identical twins. That this is so has long been alternately suspected and denied, and decisive proof came only with the late war. Extensive skin destruction is a common consequence of severe burns, and natural proliferation of epithelial cells from the boundaries of the damaged area is inadequate to repair the loss. But successful new growth of skin epithelium can be obtained if numerous small skin slices or " buttons " are taken from an intact part of the patient's body and distributed at intervals over the damaged area. The small donor areas are repaired by natural overgrowth, and epithelium grows out laterally from each transplanted fragment over the raw area, and a complete new covering is formed. But if similar fragments taken from any other human being are employed they are, in the course of days or weeks, inevitably destroyed and eliminated by a reaction provoked in the body of the recipient (Gibson and Medawar, *J. Anat.*, 1943, **77**, 299; Me awar, *Bull. War Med.*, 1943, **4**, 1). A similar problem faced those surgeons who had to deal with the extensive gaps sometimes produced in peripheral nerve trunks by the massive wounds of warfare. These gaps can successfully be closed by a graft of nervous tissue taken from another part of the patient's body; the transplanted nerve serves as a bridge down which the regenerating nerve fibres can pass to the muscles and sense organs that they serve, and function is restored. But homografts—those taken from another human being—are totally unsuccessful (Seddon and Holmes, *Surg. Gynec. and Obst.*, 1944, **79**, 342).

This manifestation of individuality within a species naturally recalls a much older instance, that of the human blood groups. For the last 300 years blood transfusion has been attempted as a method of saving life, and Keynes has related the strange history of these attempts (*Brit. J. Surg.*, 1943, **31**, 38). But it was found that indiscriminate transfusion of blood from one human being to another was often followed by severe shock or death of the recipient. This reaction is the consequence of the " clumping " (agglutination) of the transfused red corpuscles by a reaction between antigens (agglutinogens) present in the red corpuscles of the transfused blood and antibodies (agglutinins) present in the serum of the recipient. At the beginning of this century Landsteiner showed that human beings can be divided into four groups with respect to the agglutinogens present in their red corpuscles: A group contain the antigen A, B group the antigen B, AB group have both antigens and O group neither. Every individual contains in his serum the antibodies

(known by the corresponding Greek letters α and β) which will react with the antigens absent from his own corpuscles. Transfusion of blood from, for example, an individual of group A to an individual of group B results in a reaction between the antigen A in the donor corpuscles and the antibody α in the recipient serum.

Antigens other than those of the ABO group have recently been discovered also to be present in human blood; they differ, however, from those of the ABO group in that the corresponding antibodies are not normally present in the serum (see Race, *Brit. Med. Bull.*, 1946, **4**, 188). But such antigens possess the power, when transfused, of causing the formation *de novo* of the antibodies with which they can react; so arises the important distinction between *innate* and *acquired* immunity. The ABO antibodies are ready-made, and a transfusion reaction is immediate; those of the other groups are only made to measure, and the immune reaction is delayed. Hence immunity to transfusion of blood of these other groups is acquired by the same mechanism as that by which immunity to an infectious disease may develop; in the latter case the invading organisms or the toxins that they form act as an antigen; a corresponding antibody is formed during the course of the first attack of the disease, and at the next invasion there is an immediate reaction between the antigen and the antibody now present—the subject has become immune or at least more resistant to the disease.

It has been shown that differences between individuals with regard to the possession of blood antigens of all groups are inherited in a straightforward Mendelian fashion (see Race, *supra*). Thus in the case of the ABO system (now divided, in point of fact, into A_1, A_2, A_3, B and O) one gene of a multiple allelomorphic series corresponds to each one antigen. Since two genes of such a series must always be present in the diploid chromosomes, a human being may belong to any one of 15 genetic groups with regard to his ABO inheritance. Blood group characters are one of the best examples of hereditary characters whose expression is directly determined by the genetic make-up of the individual, for they are not normally modified or masked either by environmental factors or by the effect of other genes in the nucleus. Hence blood-grouping is particularly well suited to genetic analysis, and Irwin and his colleagues have been able to make a precise analysis of the inheritance of numerous blood antigens in pigeons and doves (*Amer. Naturalist*, 1943, **77**, 211; *J. Immunol.*, 1943, **46**, 63). It was found, with certain exceptions that need not be described here, that each antigen is determined by a single gene, and that each gene deter-

mining the presence of a specific antigen acts without modification by any other gene in the chromosomes. This reminds us of an important suggestion first made by Haldane some years ago and now affirmed by Sturtevant (*Proc. Nat. Acad. Sci. U.S.A.*, 1944, **30,** 176); that is, that since there is a one-to-one correspondence between antigens and single genes, and no gene interaction, then antigens may be regarded as *direct gene products.*

Now, antigens have the power to elicit and to react with antibodies; if they are direct gene products it is likely that there is a close structural resemblance between antigen and gene molecules. May it not be found, suggests Sturtevant, that antibodies will react directly with the parent genes? This reaction, if it has any effect at all, must presumably modify the structure of the gene; if so, the modification will be transmitted to all genes produced by the duplication of the affected parent in nuclear division, and it is therefore a mutation. Can antibodies produce gene mutations?—Emerson has tested the possibility with suggestive results (*Proc. Nat. Acad. Sci. U.S.A.*, 1944, **30,** 179); if it can be proved true, then the geneticist and embryologist will be given a most powerful weapon for their analytical armoury: a single gene-determined process may be inhibited, and the consequences of this inhibition followed at every step.

The complex and improbable chemical reactions by which a living organism is elaborated from a single cell are largely controlled by enzyme action; is it possible to correlate the presence of specific genes with the presence of specific enzymes? This has been done by Tatum and Beadle (*Ann. Missouri Bot. Gard.*, 1945, **32,** 125). They have correlated the pattern of inheritance with biochemical activity in the ascomycete fungus *Neurospora*: they produced mutations in single genes by irradiation, and the biochemical activities of the normal and mutant individuals gave evidence that the presence of specific single genes determines the presence of specific single enzymes. Biochemical syntheses in which more than one enzyme are concerned are controlled by a corresponding number of genes, and the authors conclude that "the genes concerned in biosyntheses, and probably all genes, act in a primary way by determining the specificity of, or in controlling the production of, enzymes." It may be noted that this view of the gene-enzyme relationship offers a clue to the understanding of the phenomena of gene interaction which often tend to confuse the elementary study of genetics: the effects of separate single genes must be "mixed up together" if each gene determines one step in an elaborate chain of reactions. That is, that the modification of the action of one

gene by that of another is not an exception to the general rule of the correspondence between unit factors and unit characters ; it means only that the unit characters are on the biochemical rather than the morphological level.

A third line of work, on inheritance in varieties of yeasts, has not only shown that here also the enzymes, concerned in fermentations, may be regarded as primary gene products, but also that, in some cases, the enzyme molecules are capable of self-duplication in the absence of the parent gene, so long as the substrate necessary for the reaction is present. This power, which is incidentally the prime criterion of life, is essentially gene-like, for every gene must duplicate itself at cell-division. In one sense, therefore, genes themselves may be regarded as "potential enzymes" (Lindegren and Spiegelman, *Ann. Missouri Bot. Gard.*, 1945, **32,** 107 and 139 ; Lindegren, *Proc. Nat. Acad. Sci. U.S.A.*, 1946, **32,** 68).

The above conclusions show the relevance and promise of the investigation of skin grafting, for the reaction to foreign skin is clearly an immune reaction. Medawar has shown that skin grafted from one rabbit to another produces a systemic reaction in the recipient that has all the characters of an actively acquired immunity (*J. Anat.*, 1944, **78,** 176 ; *J. Anat.*, 1945, **79,** 157). The survival time of the transplanted skin varies inversely with the quantity of skin grafted, and it is less when the rabbit that receives it has been grafted on an earlier occasion with skin from the same donor. The genetics of the antigens concerned are much more complicated than is the case with the blood group antigens : Medawar demonstrated that there are *at least* seven antigens concerned, randomly combined in at least 127 "skin transplantation groups." In reality there are probably many more, perhaps as many skin groups as there are individual rabbits. Although there is a family resemblance between the antigens of blood and skin they are, in fact, quite distinct ; the old view that skin homografts might be successful if sufficient attention were paid to the correct blood grouping of donor and recipient may now be dismissed (Medawar, *Brit. J. Exp. Pathol.*, 1946, **27,** 15). Medawar has given us good reason to believe that the antibodies that react with the antigens in foreign skin react only on the foreign cells in the course of their division (*Brit. J. Exp. Pathol.*, 1946, **27,** 9). This view may be interpreted to mean that the antibodies act specifically on those ingredients of the cell that are actively reproducing themselves at cell-division ; that is, upon the genes themselves, and perhaps also upon the self-reproducing enzymes of the cytoplasm (the general occurrence of the latter must be postulated to account for cellular

inheritance in somatic tissue cells; see Medawar, *Brit. Med. Bull.*, 1945, **3**, 70).

It was mentioned above that "pure-lines" of laboratory animals may provide an exception to the general rule of the uniqueness of the individuals within a species. If we can produce strains, say of mice, which differ genetically from each other only by one or a few of the antigen-genes that govern the outcome of transplantation, then by interbreeding we may be able to immunise a female mouse against genes present in the embryos developing within it. By such a technique the mode of action of hereditary factors may be considerably elucidated. That such an immunisation is possible has already been shown by the discovery of the *Rhesus* antigen (Rh factor) of human blood. The Rh factor, discovered by Landsteiner and Wiener in 1940, is governed by a dominant gene. If a Rh negative woman bears a child to a Rh positive man she may become immunised against the Rh antigen absent in herself but present in the fœtus. The outcome of this is a severe and often fatal disorder, erythroblastosis fœtalis, by which not only the blood but also tissues of the child may be affected (see Cappell, *Brit. Med. J.*, 1946, **2**, 601, 641).

There is no reason to believe that the mechanism determining differences between individuals of the same species is different in kind from that separating species and the greater groupings of the animal kingdom. But the ordinary methods of genetical analysis are necessarily confined to the study of differences between individuals of an interbreeding group and cannot, therefore, be used to study the differences between, for example, rabbit and rat or rabbit and bird. But here again the study of immunity reactions has promise of a contribution. If the blood serum of an ox is injected into a rabbit, the foreign proteins of the ox serum act as antigens and affect the mechanism by which the rabbit serum protein is normally manufactured; this results in the formation of special protein molecules, the antibodies. If rabbit serum containing antibodies so formed is then mixed with ox serum in a test tube it causes precipitation of the ox serum protein. In 1904 Nuttall showed (*Blood Immunity and Blood Relationship*, Cambridge) that this "anti-ox serum rabbit immune serum" will precipitate with the serum of other animals in proportion to their zoological affinity to the ox—progressively less strongly with the series ox, sheep, pig and man. Similarly, anti-human rabbit serum precipitates less strongly with the series Anthropoids—Old World—New World monkeys. Nuttall's technique has lately been refined and greatly extended by Boyden (*Amer. Naturalist*, 1943, **77**, 234), and various

attempts have been made to apply the method to the determination of the larger animal relationships. But it is hardly surprising to find that this young technique has, as yet, done little but reinforce the conclusions of years of laborious investigation by the methods of comparative anatomy.

NOTES

A New Concept in the Quantum Theory of Radiation (R. Eisenschitz)

[Quantum mechanics of fields, I, II, III, by Born & Peng. *Proc. Roy. Soc. Edinburgh*, 1944, pp. 40–57, 92–102, 127–137.]

In classical mechanics the orbit of an electron is analysed in terms of periods all of which have to be taken into account simultaneously. In quantisation the notion of the orbit is abandoned, the single periods being assigned to different independent processes.

In classical electrodynamics and current quantum theory the field at one point is analysed in terms of plane waves all of which have to be taken into account simultaneously. In the authors' theory quantisation is carried a step further so as to abandon the notion of the field at a definite point. The single plane waves are re-interpreted in such a way that the fact of their contributing to a field quantity appropriate to the whole volume filled with radiation is an independent process. In other words a particular plane wave may or may not contribute to the total energy according to the dynamical state of the system.

The mathematical procedure which leads to this result has the merit of achieving full symmetry with regard to time and space.

Thermal equilibrium of radiation is treated according to statistical mechanics. It appears that in the range of high frequencies the amount of waves not contributing to energy is sufficient to let the total energy be finite in contrast to the infinite zero point energy of current theory.

The new method of quantisation applies also to non-linear wave equations such that they may now be employed as means of avoiding the infinite energy of electrons.

The authors show that their method of quantisation applies also to the Dirac field of electrons and the meson field.

War Work at Sheffield University (F. P. D.)

The University of Sheffield has issued a booklet giving an account of the contributions made by the various departments to the war effort. Dr. Brynmor Jones has written a very interesting account of the University's many activities, and thereby put on

record a chapter in its history at which it may well look back with satisfaction.

Advice on sources of raw materials in this country, to replace those previously imported, was one important service rendered. For instance, the discovery and assaying of new supplies of basic refractories, bonding clays and silica sands occupied the attention of the Department of Refractories throughout the war. Moreover, to relieve the railways of unnecessary transport, consumers were directed to the nearest sources of supplies. The Department of Fuel Technology was active in suggesting means of increased efficiency and of fuel economy to local works and hospitals. Special instructional courses were given on various subjects.

A research station was set up in the Department of Chemistry at the outbreak of war under the Ministry of Supply, with a team composed of members of the University staff and experimental officers and assistants recruited from the younger graduates of Sheffield and other Universities. The development of output in the National Filling Factories was one of their first tasks, and through elaborate studies of the flow of molten material a better control of operations was obtained, leading to a more uniform, more powerful and more economic explosive charge in large bombs and shells.

Before the war, charcoal in fuse powders was prepared from specially imported wood. The Botanical Department undertook a survey of the stocks of the Alder Buckthorn (*Rhamnus frangula*) growing in England, and the Chemical Research Team, together with their botanical colleagues, carried out extensive investigations of this and other woods and their carbonising properties.

With the development of Radar, the Physics Department was engaged on improvement of the equipment, and especially on the design, development and production of special permanent magnets, which form an essential part of the "Magnetron" valve.

The Department of Glass Technology was engaged on many problems, such as increasing the resistance of bullet-protecting laminated glass and the designing of a glass ampoule, employed in a special device for firing aircraft bombs.

The Department of Metallurgy undertook an investigation into the improvement of the surface finish of small steel castings, and also on the defects in a great number of armament components, such as springs, gun barrels and automatic weapons.

Production of components for the Ministry of Supply and the Ministry of Aircraft Production was the main work of the Engineering Department, and the total output of gauges, cocking handles

and sear bars for the Sten gun, and exploder rings for shells, was nearly 1,400,000.

The Medical Departments were also fully engaged. The Department of Bacteriology was responsible for the distribution of both military and civilian supplies of penicillin in the district, and for the bacteriological control of the new treatment. A research unit was formed in the Department of Pathology to deal with traumatic shock, and the team was constituted a full R.A.M.C. unit, eventually being attached to the 21st Army Group to deal with casualties from the Battle of the Rhine.

The Department of Zoology carried out tests in connection with the sea rescue service of the R.A.F. to determine how long crews could survive with no or very little water. Important work on the prevention of scabies was also undertaken. Nutritional surveys were carried out by the Department of Biochemistry.

The Department of Education arranged lectures and classes for members of H.M. Forces, while the Engineering Department instituted special courses for training engineers, and the Physics Department for training personnel to operate Radar equipment.

Many of the staff were seconded to Government Departments for important war work, and the above brief summary will show that the University fully played its part in the strenuous years through which we have lived.

The Magnetron as a Generator of Centimeter Waves. (Developments at the Bell Telephone Laboratories, 1940–45.) (G. S. Brayshaw)

[J. B. Fisk, H. D. Hagstrum and P. L. Hartman, *Bell System Technical Journal*, **25**, No. 2, April 1946.]

An essential feature of any precision long-range radar system is a radio frequency oscillator capable of delivering high-peak powers at extremely high radio frequencies. In 1939 the lack of such an oscillator prevented any outstanding improvement being made in the existing radar equipment. Thus the development in this country by J. T. Randall and H. A. H. Boot of their cavity or multi-resonator magnetron oscillator, which was capable of a much greater peak output at very short wavelengths than any existing device, represented a major step forward. Owing to the importance of this new oscillator and its great potentialities for further improvement, it was extensively investigated by various research teams. In particular an investigation was made at the Bell Telephone Laboratories' radio laboratory at Whippany, N.J., U.S.A. Their test of the cavity magnetron submitted showed that it could supply

peak powers several times as great as those obtainable with their best existing triode oscillators, at a frequency four times as great. From this start considerable research was conducted by the Bell Telephone Laboratories, and the April number of their Technical Journal gives a comprehensive account of this work.

The discussion is divided into two parts. Part I comprises 95 pages and is concerned with a general discussion of present knowledge relating to the magnetron oscillator. To many readers this may be the most useful part, as it represents an authoritative summary of the new information gained from the wartime research carried out by the various allied workers. Such work has until recently been secret and its publication now is likely to be of considerable interest to those who did not have access to this information during the war. Part II comprises 85 pages and deals with the actual developmental work on the magnetron oscillation carried out at the Bell Laboratories during the period 1940–45. This work included the investigation and development of many different types of magnetrons with wavelengths covering the range 45 cm. to 1 cm., and with peak powers in some cases exceeding one megawatt. The complete account gives an impressive picture of applied research and engineering directed to the solution of an urgent problem.

It is not proposed to review here the contents of this paper in any detail, but it may be of some interest to discuss briefly the main features of the multi-resonant magnetron and to give a simplified explanation of its mode of operation.

A magnetron is defined as a thermionic valve whose behaviour is dependent upon a magnetic as well as an electric field. Such a system was first investigated by Hull [1] in 1921. Hull used a diode consisting of a cylindrical anode with an axial filament and having a magnetic field parallel to the filament. However, in Hull's arrangement the magnet winding is coupled to the plate circuit, and hence his system is not suitable for radio frequency oscillations. In the more modern types of simple magnetrons used for ultra-high radio frequencies the oscillation depends on electron inertia effects, and no coupling is used. In this case the electric and magnetic fields are adjusted, so that the time taken for the electrons to move from the cathode to the anode and back is equal to or nearly equal to the oscillation period of the oscillatory circuit.

Now the performance of any type of R.F. magnetron oscillator depends on the interaction of the emitted electrons, which are subjected to the constraints of the unidirectional axial magnetic field and the unidirectional radial electric field, with the superposed

[1] A. W. Hull, *Phys. Rev.*, **18**, 31, July 1921.

radio frequency field. For R.F. oscillations to be generated it is necessary that more energy should be given up by the "favourable" electrons to the R.F. field than is extracted by the "unfavourable" electrons from this field. The efficiency of oscillation will naturally depend on the extent to which the former energy transfer exceeds the latter, and the success of the multi-resonant magnetron is due to the fact that the electron path is such that the maximum favourable transfer of energy occurs. This is achieved by constructing the anode of the magnetron in the form of an annulus containing R.F. resonant cavities. Hence, when the constraining electric and magnetic fields are adjusted so that the electrons follow an approximately epicycloidal path in the space between the cathode and anode, the electrons pass through a series of R.F. fields which are themselves varying in the form of a standing wave. The motion of the R.F. fields is arranged so that their phase relationships relative to the electrons are in the proper sequence for the transfer of energy to favourable electrons to occur over a comparatively long period of time, whilst that to unfavourable electrons takes place in a relatively short time.

Since the R.F. resonant frequencies depend on the physical dimensions of the cavities, the magnetron oscillator cannot readily be used as a variable frequency generator. Nevertheless, adjustments over small frequency ranges are possible, and these and many other practical problems are discussed in the paper.

Indian Nutrition (Geoffrey H. Bourne)

1. Inadequate Diets, Deaths and Diseases and a Food Plan for Madras. By K. G. Sivaswamy. Nutritional Diseases. By Dr. M. P. Chacko. Food Hints. By Dr. S. Gurubatham. [Pp. 72 + 12.] (Royapettah, Madras: Servants of India Society, 1946. Rs. 2.–.)
2. Famine, Rationing and Food Policy in Cochin. By K. G. Sivaswamy. Medical Surveys. By Lt.-Col. T. S. Shastry and Dr. J. A. Bhat. [Pp. x + 78 + 35, with 8 plates.] (Royapettah, Madras: Servindia Kerala Relief Centre, 1946. Rs. 3.–.)
3. Food Control and Nutrition Surveys, Malabar and S. Kanara. By K. G. Sivaswamy, the late V. R. Nayanar, Dr. R. G. Kakade, and L. N. Rao. Diet and Disease Surveys. By Eleven Doctors. [Pp. 225, with 7 illustrations.] (Royapettah, Madras: Servindia Kerala Relief Centre, 1946. Rs. 4.–.)
4. Food Famine and Nutritional Diseases in Travancore (1943–44). Surveys by K. G. Sivaswamy, K. K. Chandy, Lt.-Col. T. S. Shastry, Dr. M. E. Naidu, Dr. T. V. S. Shastry, and 7 other doctors. [Pp. 264, with 33 illustrations.] (Servindia Kerala Relief Centre, 1945. Rs. 5.–.)

India is a country with a very large population (approximately

400 million). Such a population can only be fed adequately if full use is made of modern methods of agriculture, *e.g.* mechanisation, collective farming, artificial fertilisation, and so on. Such methods would, of course, require less labour on the land than is at present available. Therefore, to avoid the mass unemployment which large-scale institution of modern agricultural methods would produce, there will have to be a big increase in Indian industry to take up the surplus labour. That is the Indian food problem, so to speak, in a nutshell, but it will probably be some time before it is carried into effect. The pamphlets listed above show vividly the results of the operation of the present chaotic methods of agriculture, food distribution, and price control, and are a credit to the Servants of India Society, who have been mainly instrumental, on their own initiative, in carrying out the work recorded and securing its publication.

The first pamphlet gives some illuminating vital statistics for certain parts of Madras State. During the war years there was an increase in the price of food grains, which meant that one-fifth of the population could not take up their ration, a general increase in the cost of living, a large-scale inter-district and inter-provincial movement of labour and population, all of which combined to produce a lowered nutritional state amongst the people. This lowered nutritional condition is reflected by the fact that there was an increase in the general death rate during the war years. In some districts, where the food shortage was acute, the number of deaths was almost doubled. There was a fall in birth rate and an increase in infantile mortality. The latter increased from 164 per 1000 live births in 1936 to 192·44 in 1944. Maternal mortality rose from 8·57 per 1000 births (live and still)—average for 1934–39—to 9·98 in 1944. There were also increased deaths in hospitals and increased incidence in diseases such as cholera, amœbic and bacillary dysentery, diarrhœa, malaria, scabies, dropsy and "ulcerative inflammation," in addition to increases in diseases due directly to vitamin or other nutritional deficiency. The other portions of the pamphlet deal with a food plan for Madras and with the nutritive value of different foods.

The second pamphlet deals with the evolution in food control in Cochin, problems of rationing and so on. A series of appendices are provided which give, amongst other valuable information, vital statistics which support those given in the first pamphlet. Pamphlets 3 and 4, which provide similar material to that given in pamphlet 1, for Malabar and S. Kanara and for Travancore, tell the same story.

There is room for improvement in setting out and printing these

pamphlets, and some of the nutritional statements made are not accurate, but the important thing is that the work has been done and, more important, has been published. This is the sort of investigation that should be backed financially and extended all over the country by the Indian Government, which should also act upon many of the recommendations made by the authors of these pamphlets.

Miscellanea

Mr. G. Heyworth, chairman of Lever Bros. and Unilever, Ltd., has been appointed chairman of the Advisory Council for Scientific and Industrial Research, in succession to Lord Riverdale. Prof. H. W. Melville, professor of chemistry in the University of Aberdeen, has been appointed a member of the Council, in succession to Sir Franklin Sibly.

Prof. C. H. Lander, who has just retired from the chair of mechanical engineering at the City and Guilds College, University of London, has been appointed dean of the Military College of Science.

Mr. H. J. Page, M.B.E., has been appointed principal of the Imperial College of Tropical Agriculture, in succession to Mr. O. T. Faulkner.

The National Coal Board has appointed Prof. D. Hay, president of the Institution of Mining Engineers, to be chief mining engineer to the Board, and Dr. Jacob Bakker, of the Netherlands State Coal-mines, has joined the Board as adviser.

The following University appointments have been announced: Dr. A. C. Aitken, F.R.S., professor of mathematics in the University of Edinburgh; Prof. R. N. Arnold, regius professor of engineering in the University of Edinburgh; Dr. F. Bell, professor of chemistry at the Belfast College of Technology; Dr. E. T. Davies, professor of mathematics at University College, Southampton; Mr. P. G. 'Espinasse, professor of zoology at University College, Hull; Prof. T. N. George, professor of geology in the University of Glasgow; Mr. R. D'O. Good, professor of botany at University College, Hull; Dr. F. C. Happold, professor of biochemistry in the University of Leeds; Dr. C. A. Hart, professor of surveying and photogrammetry at University College, London; Dr. S. E. Hollingworth, Yates-Goldsmid professor of geology at University College, London; Dr. Brynmor Jones, G. F. Grant professor of chemistry at University College, Hull; Dr. W. T. Marshall, professor of engineering at University College, Dundee; Dr. M. Stacey, professor of chemistry

in the University of Birmingham; Dr. E. T. S. Walton, Erasmus Smith professor of natural and experimental philosophy in the University of Dublin.

Prof. Arthur Holmes, regius professor of geology in the University of Edinburgh, has been elected a corresponding member of the Geological Society of Belgium.

We have noted with great regret the announcements of the death of the following scientific workers: Mr. G. H. J. Adlam, O.B.E., editor of *The School Science Review*; Prof. George Baborovský, professor of physical chemisty at the Technical College, Brno; Sir Louis Barnett, C.M.G., emeritus professor of surgery in the University of Otago; Sir Carruthers Beattie, formerly vice-chancellor and principal of the University of Cape Town; Mr. A. Binns, formerly chief engineer to the Port of London Authority; Prof. M. Camis, formerly professor of physiology in the Universities of Bari, Parma and Bologna; Sir Francis Carnegie, C.B.E., formerly chief superintendent of ordnance factories, Royal Arsenal, Woolwich; Dr. L. B. C. Cunningham, an authority on air armaments; Prof. Percy Faraday Frankland, F.R.S., emeritus professor of chemistry in the University of Birmingham; Sir Frank Heath, G.B.E., K.C.B., the first secretary to the Department of Scientific and Industrial Research; Sir James Jeans, O.M., F.R.S.; Prof. J. Laird, regius professor of moral philosophy in the University of Aberdeen; Prof. E. H. Lamb, formerly professor of civil and mechanical engineering at Queen Mary College, London; Sir Walter Langdon-Brown, emeritus professor of physic in the University of Cambridge; Mr. A. W. Lupton, senior lecturer in pharmacy and pharmaceutical chemistry in the University of Leeds; Mr. H. E. Mitton, an authority on mining research; Nikolai Morozov, honorary member of the Academy of Sciences of the U.S.S.R., scientific writer; Prof. I. Mościcki, chemist and former President of Poland; Dr. C. S. Myers, C.B.E., F.R.S., honorary scientific adviser to, and late principal of, the National Institute of Industrial Psychology; Dr. W. Payman, of the Safety in Mines Research Board; Mr. H. J. E. Peake, anthropologist; Prof. H. C. Plummer, F.R.S., formerly professor of mathematics at the Military College of Science, Woolwich; Dr. Hassan Suhrawardy, formerly vice-chancellor and dean of the Faculty of Medicine of the University of Calcutta; Mr. G. Tickner, ornithologist; Mr. H. G. Wells.

Some of the galleries of the British Museum (Natural History)

are now re-open to the public from 10 a.m. to 6 p.m. on weekdays and 2.30 to 6 p.m. on Sundays. More galleries will be re-opened as the repair of bomb damage proceeds.

The Horniman Museum, London Road, Forest Hill, London, which has been closed owing to war damage, is now re-open from 10.30 a.m. to 6 p.m. daily, except Tuesdays, and 2 to 6 p.m. on Sundays.

The British Scientific Instrument Research Association is at present engaged in putting into effect a major scheme of expansion involving the widening of its field of work, the creation of several new departments, and the establishment of new and much larger research laboratories. One of the first steps taken was the creation of an Information Department, to serve both members and staff. This department, in April 1946, began publication of a monthly bulletin containing abstracts of current literature relating to scientific instruments and other relevant matter. This bulletin is printed and most of the issues so far published have contained 16 or 20 pages. The bulletin is, of course, compiled primarily for the use of the members and staff of the Association ; but, in order that it may be of the greatest possible use to makers and users of scientific instruments, the Council of the Association has decided that it may now be supplied also to non-members, at a subscription of £2 per year. Requests for it should be sent to the Information Officer, Mr. C. W. Hanson, at the offices of the Association, 26 Russell Square, London, W.C.1.

The Scientific Film Association, 34 Soho Square, London, W.1, has recently issued a catalogue of films of general scientific interest available in Great Britain. In most cases the films are graded according to their suitability for different audiences, and a critical appraisal is given. Copies of the Catalogue can be obtained from the Association or from Aslib, 52 Bloomsbury Street, London, W.C.1, at *5s. 3d.* per copy, post free.

The United Nations Department of Public Information has issued a pamphlet dealing with *The Control of Atomic Energy* (Lake Success, N.Y., price 1*s.*). In a foreword it is stated that the report "is the product of unanimous agreement by scientists of twelve nations" and that its purpose is to consider how far effective control is possible and the methods by which such control could be achieved. It is concluded that effective control would be very difficult since it would require safeguards against the diversion of material intended

for peaceful purposes at all stages of the processes of preparation and use. It is indeed only too obvious that it will not be possible to prevent a nation—or a group of persons—possessed of the necessary raw materials from accumulating a store of concentrated nuclear fuels which could be used for evil purposes. Technologically control is feasible, whether it is possible politically is quite another matter.

The report contains an intentionally superficial account of the production and utilisation of nuclear fuels, adding nothing to the information which has been published elsewhere. There is a brief reference to one new material (uranium-233), which like plutonium-239 can be formed from uranium-238 and also from " thorium in nuclear fires burning U-235." It is stated, on the authority of the *Engineering and Mining Journal* (September 1945) that the uranium content of ores mined in 1939 amounted to about 1000 tons : enough to make from 70 to 3500 bombs or, used in power plants having an overall efficiency of 10 per cent., to produce two million kilowatt years of electrical energy.

The *Bell Laboratories' Record* for September contains an account of the search radar equipment designed and manufactured by the Laboratories for use on carrier-based aircraft. In its final form the whole apparatus weighed only 150 pounds, operated on a wavelength of 3·2 cm. and provided a radio beam less than 6° wide with an antenna aperture of only 14 inches. The antenna scanned horizontally to cover a forward sector of 150° at a frequency of 1 or 2 per second. The vertical scanning width was either 12° or 24° and the tilt of the beam could be varied by the pilot through an angle of 60°. The equipment generated pulses of radio power, at levels of 30–40 kw., lasting two-thirds of a microsecond, and a few microseconds after the emission of a pulse the receiver was ready to respond to radio echoes from objects in the antenna beam. The description is illustrated by a photograph of the equipment, but no details of the circuits are given.

The October issue of the *Journal of Scientific Instruments* contains an article by H. Huxley of the Admiralty Research Laboratory describing methods used for illuminating instrument dials. The problem is not simple. If the illumination is too great it may be visible to an enemy ; the veiling glare, if it is near the line of vision, may impair the visibility of dimly seen targets, and, if it is white, may affect very seriously the state of dark adaption of the observer's eyes. On the other hand, the illumination must be sufficient to

permit quick and accurate readings; it must be capable of control to meet varying external conditions, and, whenever it is necessary to maintain the state of dark adaption, red light must be used. The procedure adopted to meet these requirements was to lead the light to the region where it is required by a series of internal reflexions from a suitably shaped and placed piece of Perspex. For example, to illuminate a circular scale a bevelled Perspex ring is fitted round the rim of the case, a small electric lamp, surrounded by a suitable red filter, being inserted in a gap in the ring. Most of the light emerging from the ring is scattered by small irregularities on its surface, which is therefore covered with white paint except on the part facing the scale.

Another interesting paper in the same number of the *Journal*, by C. R. Barber of the National Physical Laboratory, contains a discussion of the factors which determine the brightness of tungsten filament strip lamps used for standardising optical pyrometers. The most important of these are the cooling effect due to the finite length of the filament, temperature variations along the filament due to the Thomson effect, the effect of change of room temperature, of change of sighting angle and of change of tilt (in gas-filled lamps). At present the overall accuracy of routine optical pyrometer calibrations over the range 900° C. to 1550° C. is $\pm$ 5° C., including an allowance of $\pm$ 2° C. for the uncertainty of realisation of the temperature scale in this range. It is considered that the magnitude of the remaining uncertainty can be reduced very considerably by adopting the precautions indicated in the paper.

The Cambridge University Press announces a new series of *Monographs on Modern Nuclear Physics* to be edited by Professor N. Feather and designed to provide critical accounts of work done in this field. Even in 1939 there was obvious need for monographs of this kind, and the very great volume of research carried out since that time provides ample material for books of the type now planned, even though many aspects of the subject are unfortunately still "secret." The first six volumes will be written by the Editor, Dr. S. Devons, Dr. N. Kemmer, Prof. P. B. Moon, Mr. J. Dainty and Dr. O. R. Frisch.

REVIEWS

MATHEMATICS

Theory of Lie Groups. I. By CLAUDE CHEVALLEY. [Pp. viii + 218.] (Princeton: Princeton University Press; London: Oxford University Press, 1946. 20*s*. net.)

THE author's standpoint is that General Topology has now reached a sufficiently advanced stage of development to provide a solid basis for a theory of Lie Groups in the large. This is the first exposition of Lie Groups from the modern point of view.

The book opens with an introduction to the classical linear groups, and in the second chapter the properties of groups arising from the existence in them of a topology are treated. For the study of connectedness the notion of a covering space is introduced, in terms of which a new definition of simple-connectedness is given.

Chapter III starts with an axiomatic definition of a manifold, and the notions of a tangent space, differential mapping, infinitesimal transformation, and distribution are introduced. Later in the chapter there is an example of the passage from the local to the global in the method of obtaining complete integral manifolds in the large.

In Chapter IV the concepts of manifold and group are combined to form that of an analytic group. The main idea introduced is that of a Lie Group which is defined and correlated with the algebraic notion of a Lie algebra which is associated to every analytic group.

In the fifth chapter the calculus of exterior differential forms of Cartan is applied to Lie Groups. It is shown how the forms of Maurer-Cartan can be constructed if the Lie algebra is known, leading to the construction of the law of composition in the group. At the end of the chapter, invariant integration on a group is defined, a method which is used later in the theory of compact Lie Groups and their representations which is the subject matter of Chapter VI. Early in this last chapter it is pointed out that every representation of a compact Lie Group is semi-simple. The author states in the preface that the second volume of this work will be mainly concerned with semi-simple Lie Groups.

E. T. DAVIES.

Analytical Method in Dynamics. By H. O. NEWBOULT, M.A. [Pp. viii + 81, with 16 figures.] (London: Oxford University Press, 1946. 7*s*. 6*d*. net.)

THIS book is a collection of notes on various dynamical topics, not very closely related to each other. They are discussed along lines not familiar with current text-books, which the present volume is intended to supplement, not to replace.

The first three chapters, forming three-quarters of the book, are devoted

chiefly to the use of moving axes. Chapter I considers two-dimensional problems, Chapter II three-dimensional theory, and Chapter III three-dimensional applications, including a section on applications to differential geometry. Both scalar and vector methods are used. Chapter IV considers the motion of a top, first by Lagrange's equations, and then briefly by vector methods ; Chapter V is on two-dimensional motion of a chain, and Chapter VI on Euler's equations and free rotation about a fixed point. Moving axes are little used in Chapters IV and V.

Worked examples are scattered freely in the text ; it is unfortunately not always clear where examples end and bookwork recommences. The emphasis throughout is on mathematical formulation rather than physical principles, and some of the examples seem to have been chosen solely for their mathematical interest. Mathematical interest the book certainly possesses : it should be especially interesting to university teachers of mathematics, on account of the novel modes of presentation of some of the matters considered. The author also takes great pains to clear up points often found difficult by students.

T. G. Cowling.

Leçons et Problèmes sur la Théorie des Corps Déformables. By Professor André Mercier, Dr. ès Sc. [Pp. 166, with 34 figures.] (Paris : Gauthier-Villars, 1943. Frs. 240.)

M. André Mercier is Professor of Theoretical Physics in the University of Berne. The monograph under review contains the substance of courses of lectures on elasticity and hydrodynamics delivered by the author to his students. Professor Mercier remarks, however, that the logical presentation in his book does not follow the sequence in which the various aspects of the subject are introduced in class. A more empirical approach is there adopted.

The presentation is divided into three sections. In the first of these the general theory of deformable bodies and media is built up and a special point is made of developing a general stress-tensor covering the fields of classical elasticity and hydrodynamics. This tensor is a function, among other things, of (i) the space-rate-of-change of displacements and (ii) the space-rate-of-change of velocities. Special cases of the tensor which involve (i), and not (ii), are described as belonging to the field of " pure elasticity " ; those which are a function of (ii), and not (i), are described as belonging to the field of " pure viscosity." The distinction between the two fields is the one which is always made, but interest lies in the elegant mathematical synthesis of the two fields.

While building up this general theory and then showing how it separates into two special theories, the author devotes some space to the pure mathematics of Cartesian tensors. Attention is concentrated, however, upon the mathematical physics of the general problem and the author derives the stress-tensor, the deformation-tensor and the velocity-tensor in succession and then leads up to, and formulates, the general equation of motion of a body which can move, be deformed and can conduct, absorb or emit heat.

The second section concerns itself with elastic deformations and their propagation. The topics which are discussed are the significance of the coefficients of elasticity, the state of stress in two dimensions, a cylinder in torsion, a beam bent under external forces, and simple cases of wave propagation.

The first two sections take up 70 pages and the third section, of 81 pages, deals with hydrodynamics and elasticity. In it, the equation of continuity is derived, the state of stress in a fluid is discussed and the equations of motion of perfect and viscous fluid are obtained. A special case of the equations of motion is then considered and so on. The vorticity vector is defined and the question of constancy of circulation is discussed, etc. The last few pages deal with the elements of aerofoil theory.

In general, the book is clear, the exposition excellent, and the treatment mathematical and rather abstract. Only the elements of the subjects are discussed and these are dealt with in a manner rather different from that usual in this country. The book is one for those who are more interested in the formulation of general principles than in the practical aspects of hydrodynamics and elasticity.

L. Rosenhead.

ASTRONOMY

The Milky Way. By Bart J. Bok and Priscilla F. Bok. Second edition. [Pp. vi + 224, with 101 figures and 2 composite photographs in pocket.] (London: J. & A. Churchill, Ltd., 1946. 18*s*. net.)

This volume is one of the series of Harvard Books on Astronomy, edited by Harlow Shapley and Bart J. Bok, and designed to survey the various branches of the subject. The first edition appeared in 1941 in America, where also there appeared in 1945 a second edition, brought up to date by a 20-page postscript. The book is now published in this country by Messrs. Churchill. The reviewer first read the work in the American second edition. A re-reading for this review has confirmed his original opinion that this well-printed and well-illustrated volume may be recommended as a good general account of a field in which Harvard astronomers, and not least the authors and senior editor, have contributed much.

The book is popular in that it contains almost no mathematical formulæ and does not include references. Despite occasional wisecracks (the vertex of a cone is "the technical name for the place where the ice-cream drips out!"), the general treatment is thoroughly scientific and deserving of the reader's attention. The account given by Dr. and Mrs. Bok is likely to be found interesting by astronomers specialising in other fields and by the general reader who wishes to understand modern conceptions of the galaxy and the processes by which astronomers have arrived at them. The main principles and facts appear to the reviewer to be skilfully brought out in a balanced description, and it is difficult to see how a popular work could do much more in this respect. The careful reader will gain quite a large number of current ideas.

The book describes not only present knowledge, but also the plans and hopes of astronomers regarding future work. Non-astronomers may be surprised to realise how much has already been done through a substantial measure of international co-operation. It will be obvious how useful any extension of this could be. Magnitudes, spectra and colours of a million stars, with parallaxes and motions where possible, will apparently be only an instalment of the observational material with which it is hoped to extend our knowledge of the galaxy.

Alan Fletcher.

Photometric Atlas of Stellar Spectra. By W. A. Hiltner and Robley C. Williams. (Ann Arbor: University of Michigan Press; London: Oxford University Press, 1946. 42*s*. net.)

The recording microphotometer has proved a valuable aid in various spectrophotometric observations in astrophysics. The normal microphotometer tracing provides a record of the transmission of the exposed and developed photographic plate containing the spectrum, for the range of wave-length investigated. Because of the non-linear relationship between the transmission of the plate and the intensity of the light to which the plate was exposed, the conversion of the microphotometer deflections to a true scale of intensities involves heavy labour. At the Michigan Observatory a direct intensity microphotometer has been developed, which provides tracings in which the deflections are proportional to the actual light intensities. This microphotometer has been described in detail in *Pub. Observ. Univ. Mich.*, **8**, 45, 1940, so that it is not necessary to describe the method employed.

This publication contains reproductions of the intensity tracings of the spectra of eight stars obtained with the Condé spectrograph of the 82-inch reflector at the McDonald Observatory of the University of Texas. This is a Littrow type spectrograph with two prisms of Chance glass giving a linear dispersion of 2·1 A per mm. at wave-length 4000A, and of 10·0 A per mm. at wave-length 6000A. The reproductions of the tracings have been reduced in size from the original by a factor of 2, giving a resulting magnification from the original spectrograms to the published tracings of 21·6. The range of wave-length covered varies somewhat from star to star: at the short wave-length end it ranges from 3916A to 4065A and at the long wave-length end from 5908A to 6723A. The tracings are made with the continuous spectrum falling on the intensity line 100 throughout the tracing. The eight stars for which tracings are given were selected to cover as large a range of separate spectral types as possible among stars of sufficient apparent brightness. The tracings for each star are given in a separate booklet, which greatly facilitates the comparison of the same spectral region in the spectra of the various stars.

An additional booklet contains a brief description of the spectrograph, and of the application of the direct intensity microphotometer to the production of the traces. The various sources of error are discussed. Details of the spectrograms used are given and dispersion tables for each spectrogram make it possible to deduce with all necessary accuracy the wave-length at any point of each tracing.

The tracings contain a mass of interesting detail which cannot fail to prove of the greatest value to the astrophysicist.

H. S. J.

PHYSICS

Electrons in Action. By J. G. Daunt, D.Phil., M.A. [Pp. 151, with 8 plates and 22 figures.] (London: Sigma Books Ltd., 1946. 6*s*. net.)

This is the fourth of the Sigma Introductions to Science, and is intended to "give an account in everyday language of the basic principles of electricity explained in terms of the activity of electrons . . ." Dr. Daunt has largely succeeded in his aim. He assumes the reader to be an intelligent layman with no training in physical science. He employs no mathematical symbols or equations (even Ohm's Law is relegated to an appendix) and his language borders on the colloquial in places, but with the aid of effective analogies he

is able to give a very good account of the nature of electricity, its passage through solids, liquids, gases and a vacuum, and a few of the applications. The book would be read with great interest and profit by fifth- and sixth-form schoolboys, who would be stimulated to ask their physics master many questions, but the master would not have to correct misconceptions which so often result from reading over-simplified and dogmatic statements in "popular" books on science. One of the good points of this book is that the reader is left with the impression that even the highly-trained professional physicist has much to learn.

The photographs are well chosen and really do illustrate the text, but some of the line drawings are not clear and seem to miss the point. There are a few misprints and loose statements, easily corrected. Some sections could with advantage be expanded in a second edition, *e.g.* the reason for haloes in X-ray and electron diffraction photographs (p. 137).

The book can be commended to all who have to teach elementary students, and to non-physicists who wish to learn something of modern views on electricity. F. A. V.

Electrons in Action. By JAMES STOKLEY. [Pp. x + 320, with 55 figures and 37 plates.] (New York and London: McGraw Hill Book Co., Inc., 1946. 18*s*. net.)

THIS book is a "popular" account of recent applications of electrons and electron tubes. It contains no mathematics and is purely descriptive, and the author has not always escaped the consequent dangers of superficial treatment and the omission of details essential for correct understanding. The style is in some respects "journalistic" and some paragraphs read like publicity leaflets issued by firms. Nevertheless, the book contains very interesting information on recent developments and is likely to stimulate quests for further knowledge.

The scope of the book may be indicated by notes on the chapter headings. 1. "Modern Miracles"—an introduction to arouse interest. 2. "They're Called Electrons"—a very brief account of the rise of electron theory. 3. "Electrons Made Free"—thermionic and photoelectric emission. 4. "Putting Them to Work"—thermionic valves. 5. "Talking around the World"—radio. 6. "Seeing Beyond the Horizon"—television. 7. "Cosmic Electrons"—ionised layers in the atmosphere. 8. "Light from Electrons"—fluorescence and phosphorescence. 9. "Sounds for the Future"—sound recording. 10. "Electrons in Overalls"—applications of electron tubes in industry. 11. "Measurements"—various applications such as spectrophotometer, mass-spectrometer, introduction to radar. 12. "Looking through Matter"—X-rays. 13. "Smaller and Smaller"—electron microscope and electron diffraction. 14. "Electrons in Medicine"—metal detectors, measurement of brain potentials, etc. 15. "Faster and Faster"—cyclotrons, betatrons, etc. 16. "Where it leads"—a very speculative short chapter—mainly quotations. 17. "Atomic Energy"—based on the Smyth report. Appendix, "Radar"—extracts from the U.S. Government Report on Radar.

There are a number of slips, misstatements and obscurities, all of which could be corrected in a future edition. For example:—the caption of Fig. 3 is misleading, the choice of carbon for Fig. 4 is unfortunate, current is not "the number of electrons" (p. 17), Fig. 17 is quite wrong (audible sound and

supersonics are included in the E-M spectrum), Rutherford's transmutation of nitrogen to oxygen was carried out in Manchester, not Cambridge (p. 254), Cockcroft's name is wrongly spelt in several places.

The book is very well illustrated with diagrams and plates. Some of the plates are not very informative and might well be omitted, but others are excellent. Many of the diagrams are reprinted from Dunning and Paxton's *Matter, Energy and Radiation*. The publishers have done their work well, as usual.

F. A. V.

The Cathode Ray Oscillograph in Industry. By W. Wilson, D.Sc., B.E., M.I.E.E. Second edition. [Pp. xii + 244, with frontispiece and 194 figures.] (London: Chapman & Hall, Ltd., 1946. 18*s*. net.)

The second edition of Dr. Wilson's book is a well-produced, and, as far as is possible in these days of ultra-rapid progress in all matters technical, an up-to-the-minute account of the many industrial applications of the C.R.O., and as such should prove of great value to technicians in almost every branch of science and engineering.

The circuits included are very useful and the numerous photographs of both apparatus and recordings give an exceedingly valuable indication of the potentialities of this instrument to industry generally. I find the book very enjoyable reading—which for a text-book is a great asset.

The first four chapters, which deal with the basic principles of the oscillograph, pay very little attention, as the author states in his preface, to fundamental theory. This is an admirable decision in my opinion, as otherwise the book would of necessity be longer and more complicated, so that its appeal to the majority of readers for whom it is intended, namely actual and potential users of the C.R.O., would be reduced. The lack of fundamental work, however, causes a certain looseness of phraseology to creep into one or two explanations. For whilst points like kilometres per second, miles per second, or centimetres per micro-second are matters of opinion, the author is wrong when he describes the anode diaphragm as an electron gun. The whole of the beam-producing system (excluding the deflector plates) is usually referred to by this term. Further, I do not like the term of "cathode oscillograph" which occurs from time to time. What is wrong with the usual abbreviation "C.R.O."?

On the other hand, the practical applications covered in Chapters 5 to 9 more than compensate for these slight disadvantages. The clarity of the text, the lucidity of the descriptions and the variety of tests covered, together with the large number of illustrations, all serve to make the practical part of the book very impressive. The only criticism here is that the author seems to make the application of the C.R.O. to a large number of widely different problems almost too easy. As the Head of the development laboratory of a large industrial concern, the author is obviously well versed in these matters and would be the first to admit that some experience is necessary before it can be definitely known that the picture on the screen is exactly the quantity it is intended to measure. There is no denying that the results which are illustrated in the book can be obtained, but I think some warning of the pit-falls and possible errors would have added considerable value. For instance, the necessity for screening to avoid either direct or radiated pick-up cannot be ignored, particularly when dealing with

high-voltage or high-frequency phenomena and, unless the pick-up is obvious, the picture on the tube can lead to very misleading results.

The electron microscope section, although well written, cannot do more than touch on such a vast specialised subject and could perhaps have been omitted for the reason that it is just as specialised as television, which the author himself has deemed to be outside the scope of the book. Nevertheless, the non-specialist will find it an interesting and informative survey of the applications of this development in electronics.

For the benefit of those who are familiar with the first edition, a number of other applications have been included such as the Supersonic Flaw Detector, the determination of Young's Modulus by measuring the frequency of longitudinal vibrations, Steel Sorting and a Strain Gauge Pick-up. Although the additions are of a rather specialised nature they serve to make the book more complete. Chapter 2 has been enlarged to deal with the "Magic Eye" and Chapter 12 on Construction, Operation and Maintenance has been improved by the addition of information on the photographic aspect of single-sweep high-speed traces. Finally, the general layout has been revised and the illustrations re-arranged so that the second edition is generally more readable.

F. W. T.

Hydraulic Measurements: A Manual for Engineers. By Professor Herbert Addison, M.Sc., M.I.Mech.E., A.M.Inst.C.E. Second edition. [Pp. xii + 327, with 158 figures, including 4 plates.] (London: Chapman & Hall, Ltd., 1946. 21*s*. net.)

In the preface to the first edition of this work the author explained that the adequacy of the corresponding chapter in his text on Applied Hydraulics had been questioned by some reviewers. If this is the cause of Prof. Addison's present book, clearly reviewers have their uses. His Applied Hydraulics set a new standard indeed for students' books and, although the present text is written for engineers rather than students, it sets an equally high standard.

Many technical papers have been written on the subject, the author himself giving no less than 214 references, but there was apparently no text covering the whole field, and this treatise, now in its second edition, must help to meet the need.

The measurement of the flow of water is becoming of more and more importance to the engineers of the various drainage boards, hydro-electric plants and the water supply of towns. To all engaged in such works a compendium of the many metering devices should be welcome.

It is difficult to discover any sound method of measurement which is not described. One exception, however, is the so-called "collar-stud" notch, in which the width of opening is so proportioned relatively to the height over the sill that the rate of discharge varies directly as the head. The advantage of this device is the resulting simplicity of the integrating mechanism.

Not only are the standard metering gears such as Pitot tubes, Venturi meters, notches, vane and current meters and the use of floats fully described, but several special methods are discussed, such as the standing wave and critical depth flumes, the Allen salt injection and the Gibson inertia methods. Having spent many years in Egypt, Prof. Addison is able to write with special knowledge on the use of regulating sluices, as in the Assuan Dam, and of models for the measurement of water.

The book, which has an ample supply of diagrams, may be recommended both for study and for reference. An engineer who wishes to select a suitable method of metering water can hardly fail to find in it the necessary information.

B. Lloyd-Evans.

Power. By Martin Ruhemann, D.Phil. [Pp. 123, with 8 plates and 14 figures.] (London: Sigma Books Ltd., 1946. 6*s*. net.)

This book is the fifth of the Sigma Introduction to Science Series and is a very clearly written account for the general reader of the production and utilisation of power and energy. It is intended to help in the understanding of the importance of power in our lives and of the far-reaching problems involved in the most economical generation, distribution and use of energy.

The terms "work," "force," "energy" and "power" are first defined in the technical sense, and then there is a description of the rôle played by tools and machinery. The various sources of energy are reviewed, including coal, oil, running water and (briefly) atomic energy. Interesting statistics are given as to the power used in this and other countries. The processes involved in the generation and distribution of electricity are described. Nowhere is the argument obscured for the non-scientist by the use of more technical terms than necessary, or by any mathematical symbols. Dr. Ruhemann's style is easy, and the text is enlivened by amusing and telling drawings by Victor Reinganum. The plates are illustrative in the newspaper sense rather than the technical.

The book can be commended to anyone interested in the broad issues involved, and should find a place in public and school libraries.

F. A. V.

Elementary Theory of Gas Turbines and Jet Propulsion. By J. G. Keenan. [Pp. viii + 261, with frontispiece and 194 figures, including 5 plates.] (London: Oxford University Press, 1946. 15*s*. net.)

The first patent for a gas turbine was granted as early as 1791, but development has been slow until comparatively recently, so slow in fact that many people had not heard of this newest form of prime mover prior to the last war.

Mr. Keenan's book, giving the basic principles of this new machine, therefore comes at a most opportune moment. He has employed mathematics of about matriculation standard only and has presented his subject in a most lucid manner.

The only text with a scientific approach to the subject until the present volume appeared was Stodola's masterly treatise on *Steam and Gas Turbines*. This, however, was written before the modern machine was developed. A book explaining in simple language recent progress is clearly wanted and the author is to be congratulated on his handling of a problem which involves so much breaking of new ground.

The introductory chapter shows how two paths of attack led to the design of the modern machine; in the one, a compressed charge of gas and air was exploded in a series of chambers and the hot products allowed to play on the blades of a turbine. Each vessel was then recharged and fired in turn.

In the other form, actually the type which has survived, air alone is compressed and fuel oil burned steadily in it at constant pressure. The

two methods are to some extent analogous to those used in internal combustion engines of the explosion and Diesel types respectively.

Other chapters deal with the physics of gases, centrifugal and axial-flow compressors, including a simple discussion of surging, combustion chambers, the theory of nozzles, impulse and reaction turbines and heat exchangers, all essential parts of the modern gas turbine.

The questions of efficiency and performance are discussed in some detail, also the application of the turbine to jet propulsion. The consumption figures quoted indicate that considerable research is required before such a plant can compete economically with an oil engine except under special conditions such as those obtaining in the drive of an aeroplane. There is, however, fair reason to suppose that time will bring the necessary improvement. Experiments are already being made with the gas turbine locomotive.

The need for a text showing the extent of our present knowledge is obvious, and Mr. Keenan's book can be recommended to anyone who wishes to learn how far the gas turbine has now been developed. It forms an excellent introduction to the underlying theory.

B. LLOYD-EVANS.

Electricity in the Building Industry. By F. C. ORCHARD, M.I.E.E., A.M.I.Mech.E. [Pp. xii + 232, with 10 plates and 104 figures.] (London: Chapman & Hall, Ltd., 1946. 15*s*. net.)

THIS is one of a series of books for the builder on the use of electrical power. The author, with the courage of his convictions, tells us in the preface that the book will be of service for the education of operatives in the use of electrical tools. He certainly goes further than that; indeed, one might argue that for the purpose of the book he goes too deep into fundamentals. Of what use to a master-builder or his employee who wants to use an electric drill is an understanding of the Rutherford-Bohr atom or even of power factor? Either he can use the drill without troubling his head with such things or he will have gained this type of knowledge from a "straight" book on electricity.

The most useful part of the book—for the author's set purposes—deals with workshop lighting and wiring, machine and portable electric tools and their maintenance. Most interesting to the layman is the final chapter which, under the heading "Recent Research," deals with the uses of high-frequency currents, moisture meters and the drying of timber.

E. G. R.

The Diffraction of X-rays and Electrons by Free Molecules. By M. H. PIRENNE, D.Sc. [Pp. xii + 160, with 2 plates and 82 figures.] (Cambridge: at the University Press, 1946. 12*s*. 6*d*. net.)

As explained in the preface, this monograph deals chiefly with the diffraction of X-rays by gases, a subject to which the author himself has made important contributions. The influence of Debye, who writes the foreword, is evident in the book, particularly in the judicious balance between the development of theoretical ideas and the discussion of experimental investigations. By omitting details of mathematical derivations the author has been able to give in a small space a connected and critical account of all the essential principles of X-ray and fast-electron scattering and of their application to the determination of molecular structure; this account, as a concise summary of available knowledge, will be useful to students of X-ray physics in particular, but its

chief appeal will probably be to the much larger circle of those interested in the problem of molecular structure in general. Many workers in this field find it necessary to use the results obtained by techniques in which they are not specialists, and it is of the utmost importance that they should be provided with the means for forming independent judgments of the worth of such results. To these the book will be valuable, not merely for the information it contains but especially for the critical assessment which the author gives of the accuracy and limitations of the methods of X-ray and electron diffraction.

The main theme of the book, as already stated, is the diffraction of X-rays by gases; the diffraction of electrons by gases is adequately and critically dealt with, but, as is inevitable in a book of this size, the treatment of other subjects subsidiary to the principal topic is liable to be sketchy. On the whole the omissions tend to be chemical rather than physical; for example, the chapter entitled "The Chemical Bond" consists of five pages only. Similarly the critical attitude which characterises the treatment of the major theme occasionally gives place to looseness of expression elsewhere, as when the author states (p. 56) "the interatomic forces in crystals (are) not essentially different from the interatomic forces which build up molecules."

There is a good bibliography, and the book is well produced and free from typographical errors. An addition which would add to the value of the book in a subsequent edition, particularly to less advanced students, would be the insertion of a few paragraphs, probably after Chapter III, summarising and correlating the various aspects of the interaction of X-rays with electrons and atoms which have been dealt with separately in the first three chapters. It is customary to deal with coherent scattering primarily from the classical point of view, and with incoherent scattering and fluorescence as quantum phenomena, so that it is sometimes difficult for the student to obtain the integrated picture of them which such a summary could provide.

E. G. Cox.

CHEMISTRY

Physical Chemistry for Colleges. By E. B. Millard. Sixth edition. [Pp. ix + 682, with 72 figures.] (New York and London: McGraw-Hill Publishing Co., Ltd., 1946. 22*s*. 6*d*. net.)

The aim of this book is stated in the preface to be that of "Presenting physical chemistry to beginners with such simplicity that they can understand it after careful study, and yet with such precision that they will acquire a sound background with which to continue in the field beyond the introductory course." In this respect the book succeeds, and as in the present edition it has been extensively rewritten and brought up-to-date it gives a good outline of the subject up to about Pass Degree or General Degree standard.

At the same time it leaves one with the wish that the exigencies of space had permitted certain subjects to have been followed up a little more deeply so as to give a better balanced review of the topics treated. Thus the chapter on Colloids deals only with certain aspects of the subject, for instance although McBain's work on soaps is reviewed briefly no mention is made of Hartley's important studies of paraffin chain salts. The important principles of catalytic action and the mechanism of heterogeneous reactions are also left unmentioned. The book is, however, provided with sufficient references

to more advanced works and to selected original papers to stimulate the student who becomes particularly interested in any branch to pursue his studies further.

The thermodynamic section of the subject is extremely well treated, and gives a good introduction to the subject in a simple but accurate manner. For British students it is unfortunate that the symbol F is retained for Gibbs's Free Energy instead of G, the symbol agreed at the 1937 meeting of British and American scientific societies.

A particularly useful feature of the book is the wealth of numerical examples, many being taken directly from the chemical literature, the solution of which should assist the student in the understanding of the subject. The printing, binding and general production of the book are well up to the usual high standard of the McGraw-Hill Co.

J. W. SMITH.

The Chemistry of Free Radicals. By W. A. WATERS. [Pp. viii + 295, with 24 figures.] (Oxford: at the Clarendon Press, 1946. 20*s*. net.)

ONE of the main objectives of organic chemistry concerns the elucidation of the fundamental laws which govern the relationship between constitution and reactivity, so that ultimately it may be possible to predict in detail the chemical properties of complex structures. Although considerable advances have already been made towards this objective, more particularly by the classical investigations of Lapworth, Robinson and Ingold, it has become realised more recently that these theories based on an electronic interpretation, though of very wide application, by no means cover the whole field. During the past ten years there has emerged the realisation that many reactions involve atoms and free radicals, and the logical development of this field has brought to light new preparative processes and a more intimate understanding of many important phenomena. The experimental evidence for the existence of atoms and free radicals, and the mechanisms of the reactions in which they participate, form the subject of Dr. Waters's book.

The earlier chapters deal with the classical work on the stable radicals of the triphenylmethyl type and the later discovery of the free alkyl radicals of short life, and these are followed by chapters on the magnetic properties of free radicals, free radicals based on elements other than carbon, and photochemical decompositions. Although certain gaseous reactions are mentioned, the main content of the book is devoted to reactions involving atoms and free radicals in solution, an aspect of the subject on which the author himself was one of the pioneer workers. Perhaps the most important consequence of the theory of free radical reactions is the fact that such radicals and atoms can act as catalysts for certain addition and substitution reactions, and also for the chain polymerisation of olefines. These applications, which are frequently of considerable industrial importance, are reviewed in detail. The final chapters are devoted to oxidation and some possible mechanisms for biological processes and, though more speculative in character, they serve to show the wide implications of the subject and to direct attention to many problems which call for further investigation.

In *The Chemistry of Free Radicals* Dr. Waters presents the first account of developments in an important and rapidly developing field, and he writes in that clear and convincing style which makes his books always a pleasure

to read. This book is invaluable as a reference work, and should be read by all who are interested, whether as teachers, students or research workers, in the mechanism of organic reactions and the more physical aspect of organic chemistry. It is presented in the usual high standards associated with the publications of the Clarendon Press and is very reasonably priced at 20*s*.

D. H. H.

The Chemistry of the Acetylenic Compounds. Vol. I: The Acetylenic Alcohols. By A. W. Johnson, Ph.D. [Pp. xx + 394.] (London: Edward Arnold & Co., 1946. 35*s*. net.)

The importance of acetylene as a basic material for chemical industry has increased to such an extent in recent years that it may now be said to challenge benzene for pride of place as the organic compound of greatest importance in industry. The subject matter of the three volumes on *The Chemistry of the Acetylenic Compounds* planned by Dr. A. W. Johnson is, therefore, of major importance, and the publication of the first volume on *The Acetylenic Alcohols* is a timely and welcome event. Apart from certain American publications primarily concerned with the acetylenic hydrocarbons, there appear to be no comprehensive reference works devoted to the chemistry of acetylenic derivatives in a broader sense.

The present volume is confined to the Acetylenic Alcohols, including the monohydric, dihydric and polyhydric alcohols, as well as the polyacetylenic alcohols. Each section, which is presented in a systematic and logical manner, includes an historical survey and detailed information on methods of preparation, physical properties and reactions. The systematic presentation adopted by Dr. Johnson frequently leads to some repetition. For example, the Reformatsky-type reaction between propargyl bromide and *cyclo*hexanone is mentioned, complete with formulæ, at least three times (on pp. 11, 68 and 141). In similar manner the hydrogenation of Zeile and Meyer's glycol is set out on p. 156 and again on p. 195. Such duplication is not altogether a disadvantage, since it makes it the easier for the reader to find the information he is seeking. In order to avoid breaking the continuity of the main body of the work, appendices are included on The Chemistry of the Rubenes, Acetylenic Alcohols in the Sex Hormone Series, and on more recent advances up to September 1945. A further appendix gives the principal physical constants and literature references to the best-known methods of preparation for all known acetylenic alcohols, under a formula index based on the Richter system. This book contains a large mass of information which is fully documented throughout with original references and presented in a clear and concise manner with ample structural formulæ and diagrams.

This volume and its sequels will constitute an invaluable reference work, and chemists and others will be grateful to Dr. Johnson for having collected and catalogued so much useful information in such an accessible form. Both the author and the publishers are to be congratulated on the production of this volume under the stress and trials of the past few years when, as Sir Ian Heilbron aptly states in his foreword, it must have required considerable determination and optimism to embark on a task of this magnitude.

D. H. H.

Advances in Carbohydrate Chemistry. Vol. I. Edited by W. W. Pigman and M. L. Wolfrom. [Pp. xii + 374.] (New York: Academic Press, Inc., 1945. $6.00.)

Although in recent years the intriguing study of carbohydrate chemistry has attracted increasing numbers of academic and industrial research workers, there has been no publication in which their individual contributions could be collected, sifted and critically examined in the necessary length and detail which the subject warrants. It is inevitable, therefore, that they should welcome the appearance of this volume, which is the first of a series to be published annually in an effort to satisfy this vital need, and for which credit must be given to the initiative and enthusiasm of a small group of American and English workers.

This first volume, in which each chapter has been written by a recognised expert at the invitation of the committee, is mainly of an academic character, but industrial aspects will be reviewed in later volumes. The wide range of subjects discussed includes orthoesters, thio- and seleno-sugars, cardiac glycosides, sugar alcohols, nucleic acids, starch, cellulose and plant polyuronides. Appropriately, pride of place is given to modern developments of Fischer's "Cyanohydrin Synthesis."

In general, the presentation is such that there is available an abundance of valuable information for the specialist without obscuring those fundamental aspects which are of interest to a wider scientific public. An important feature of the book is the frequent reference to current controversial problems and the expression of personal viewpoints by the individual authors on such problems.

The editors need not fear that their readers will be adversely critical of this first volume or that the *Advances* will not receive the whole-hearted support of carbohydrate chemists. Nevertheless, as they welcome constructive suggestions, one is tempted to propose that references should be grouped at the end of each chapter rather than at the foot of each page.

The reviewer also feels that mention of unpublished work should be avoided, since space considerations do not permit the inclusion of sufficient experimental detail to enable the value of such work to be assessed. Perhaps this is only a passing phase, attributable to a desire to eliminate the long delays in post-war publication through the usual channels.

The publishers are to be congratulated for extending their current series of invaluable reviews into the realm of sugar chemistry, especially since the English-speaking chemist is now able to enjoy the luxury of keeping his knowledge up to date without the necessity of delving into German *Fortschritte*.

If the high standard of Volume I is maintained in subsequent volumes, then indeed, as the editors hope, a comprehensive survey of the development of carbohydrate chemistry will be available in later years.

Edward J. Bourne.

Advances in Protein Chemistry. Vol. II. Edited by M. L. Anson and John T. Edsall. [Pp. xiv + 443, with 14 figures.] (New York: Academic Press, Inc., 1945. $6.50.)

During recent years the problems of protein chemistry have been studied by workers in many different fields of Biology, Chemistry and Physics, and progress in the subject has become so rapid as to make possible the production

of this series of volumes in which various workers may present their views in an organised form and express their personal judgment on controversial subjects. Most of the articles are more in the nature of reviews on special aspects of Protein Chemistry, rather than elaboration of theories. It may be that the production of this series of volumes is somewhat premature, especially if they are to appear yearly, since some of the subjects do not seem sufficiently advanced to warrant an extended treatment, and others have been reviewed elsewhere. However, it is better to read the same thing twice than not at all, and this series of articles is extremely interesting, and should be of especial value to research workers and advanced students concerned.

The first volume dealt mainly with proteins as they occur in nature. Many different subjects are reviewed in the present volume, while special emphasis is laid on the nutritive properties of proteins. These are dependent on the amino-acid composition, which is the subject of the first three articles. A. J. P. Martin and R. L. M. Synge give a comprehensive account of methods of amino-acid analysis, followed by an almost complete bibliography of 771 references, which should be of great use to the analyst in this field. A method of analysis which promises to be of great use in the future is the microbiological method, which is dealt with very ably by E. E. Snell. A short review on "The Amino-acid Composition of Food Proteins," by R. J. Block follows, which contains some useful tables of analyses.

The antibodies of the blood are probably one of the most important and most mysterious proteins in the body, and that their production is affected by the dietary protein is demonstrated in an article by P. R. Cannon. Two reviews deal with special types of proteins; the "Copper Proteins," by C. R. Dawson and M. F. Mallette, and the "Mucoids and Glycoproteins," by Karl Meyer. The latter is of special value as the subject has not been reviewed for many years. The large size and the complexity of the amino-acid make-up of the protein molecule mean that the action of a specific reagent on a protein may be extremely complicated. That of formaldehyde is a case in point, which is comprehensively dealt with by D. French and J. T. Edsall. The phenomenon of denaturation, for long one of the mysteries of protein chemistry, is discussed by M. L. Anson, whose account is largely concerned with the thiol groups. The subject of "X-ray Diffraction and Protein Structure," which is the last article in this volume, has been reviewed many times before. Nevertheless the present discussion by I. Fankuchen should be of especial value to the uninitiated as well as those more familiar with the field, as it deals concisely with the results of X-ray analysis, and does not attempt to draw unwarranted conclusions from them.

F. SANGER.

An Introduction to Chromatography. By T. I. WILLIAMS, B.A., B.Sc., D.Phil. [Pp. xii + 100, with 8 plates and 31 figures.] (London and Glasgow: Blackie & Son, Ltd., 1946. 10*s.* net.)

CHROMATOGRAPHY is a practical chemist's tool, characterised by an essential simplicity and almost universal applicability in separating (mainly organic) mixtures. It has seemed regrettable, therefore, that long accounts of what is often almost intuitive practice, theoretical conceptions which are remote from practicality, and numerous applications to complex organic substances should have sometimes made it appear a subject requiring much learning

before it can be profitably used. This attitude would be laughable if applied, for example, to distillation or crystallisation in their ordinary laboratory aspects; the misconception is patent to any who have witnessed its use over fifteen years since Kuhn and his associates first used it to such advantage, or who have persuaded generations of students to regard it as a day-to-day tool with minor difficulties to be circumvented by native ingenuity. Thus any present-day account of practical chromatography need only give in outline the various procedures which have been found advantageous, practical hints to assist the unwary, an indication of how theoretical conceptions may assist in devising satisfactory separations, and a few examples to afford cohesion. The present book does this very satisfyingly in 100 pages.

Principles, methods, and a few detailed examples (which might usefully have included more commonplace topics, such as dinitrophenylhydrazones, as well as somewhat remote concentrations of vitamin K_1, helvolic acid, fucoxanthin, etc.) comprises more than half the text; there are compilative directions for chromatographing colourless organic substances, inorganic materials, for partition chromatography, and a short discussion of theoretical aspects. A section on standardising alumina—a matter which is only slowly attaining the prominence it merits—is a useful feature. Some of the description is more than sufficient to enable the chemist to give chromatography a trial, and some of the plates and figures, though well produced, appear to lack point or to be inappropriate (*e.g.* Tswett's apparatus for carrying out several separations simultaneously under pressure would rarely be employed to-day). These, however, are but negative factors which do not detract from those making the book a reliable one for laboratory purposes. The only regret the book may engender is that it makes chromatography appear predominantly a tool for the biochemical laboratory with less reference to the general practice of organic chemistry.

A. H. COOK.

A Laboratory Manual of Qualitative Organic Analysis. By H. T. OPENSHAW, M.A., D.Phil.(Oxon.). [Pp. viii + 96.] (Cambridge: at the University Press, 1946. 6s. net.)

QUALITATIVE organic analysis embraces two overlapping objects; identification of common organic compounds, and interpretation of structure in a wider sense from organic reactions. Many teachers strive to impart some appreciation of the second object, whereas most books stress the first. The present work is no exception, perhaps because of limitations of size. It outlines a procedure, familiar enough in principle, for detecting characteristic groupings in a rather rigid series of tests, and an ultimate identification based mainly on the m.p. of derivatives.

If the avowed object and limitations imposed by 96 pages be remembered, this book has much to recommend it. The textual sections are clearly presented and the many tables are surprisingly informative, including data from recent literature. Details such as "petrol" and "petrol ether" may provoke minor irritation and many teachers will find notable omissions to remedy by personal instruction; examples are dealkylation of phenolic ethers, acylations in pyridine, *p*-bromophenacyl esters, acetylation of aqueous salts of aromatic amines, and hydrolysis of nitriles by alkaline hydrogen peroxide. Against such blemishes must be set features such as model bromination and nitration procedures which are admirable.

As an adjunct to qualitative organic analysis in its more comprehensive sense this book has its undoubted value as well as certain shortcomings; as a manual of more limited scope it probably represents the maximum which can be expected for its size and price.

A. H. Cook.

BOTANY

The Identification of Conifers. By A. Bruce Jackson, A.L.S. [Pp. viii + 152, with 48 figures.] (London: Edward Arnold & Co., 1946. 9s. not.)

Although the gymnosperm flora of Britain is limited to a pine, a yew and a juniper, there is a very considerable number of introduced conifers cultivated in plantations and gardens. In the past, gardeners, foresters and tree lovers have had recourse to Dallimore and Jackson's well-known *Handbook of Coniferae*, when wishing to identify one of these, but there has been a general desire for a smaller work that could be carried about in the pocket and used in the field. The handy little volume under review was written by Mr. Bruce Jackson in response to this demand and should meet with widespread approval. It is based upon the major work, to which it is intended to serve as an introduction. Compactness is achieved, partly by the omission of the less common and more tender species, but mainly by the elimination of descriptions and reliance on keys for identification. The keys to the genera and species are simple to use and, as they are based upon vegetative characters of shoots, buds and leaves, avoid the irritation so often engendered by the discovery that an identification cannot be made without cones, which are either wanting or out of reach. About half of the text is devoted to nomenclature, country of origin, size attained and short notes of arboricultural and silvicultural interest. The other half is given up to listing noteworthy specimens and their dimensions. The wisdom of taking up so much space, in a book intended largely for the student and amateur, with data easily referred to elsewhere, is questionable. If, instead, additional characters had been given, including those of the cones, the value of the book would have been augmented. In spite of the excellence of the keys there are times when supplementary information would be helpful, especially in such critical groups as the Junipers and Cypresses, where the range of variation is wide and parallel forms occur in related species. The excellent line drawings by Miss Lister clarify many details of structure and add much to the usefulness of the book.

R. M.

Trace Elements in Plants and Animals. By Walter Stiles, M.A., Sc.D., F.L.S., F.R.S. [Pp. xii + 189, with 12 figures.] (Cambridge: at the University Press, 1946. 12s. 6d. net.)

The effect of trace elements on plants and animals, rather than the actual amounts present in healthy and unhealthy individuals, is the main theme of Professor Stiles's book. The reader's attention is rightly drawn to the gap which exists between knowledge of the effects of trace constituents and ability to interpret the results of analytical determinations. The obvious need, too, for a closer study of the results of water culture experiments, on which much of our information regarding plants is based, in relation to the

conditions existing in the soil, is indicated. This might, indeed, have been further emphasised, as it is from the soil that both plants and animals ultimately derive their trace nutrients.

The presentation of the subject is useful in giving a critical survey of the present position and in pointing the way to future work. Generally, the treatment of plants is fuller than that of animals, and the historical introduction deals only with the plant aspect. An account of the deficiency diseases in plants attributable to manganese, zinc, boron, copper and molybdenum is followed by a section on the functions of these in the plant and on the interrelationship which exists in certain instances, *e.g.* between manganese and iron. A further complication which is discussed is the effect of bacteria on the trace element balance. In animals the problems of excess selenium and molybdenum and deficient copper, iodine, manganese and cobalt are dealt with.

The modern approach to the analytical problems involved in the determination of trace constituents, using absorptiometric, polarographic and spectrographic methods, is indicated in a section of the chapter dealing with all methods of investigating micro-nutrient problems.

The only misstatement noticed was to the effect that nickel has not been detected in sea-water (p. 125) and on p. 44 there is an obvious misprint of 0·3 g. for 0·3 μg. The book is eminently readable: undergraduate, research worker and general reader will all derive benefit from it, and the bibliography gives a good introduction to the literature of the subject.

R. L. Mitchell.

ZOOLOGY

The Trematoda: With Special Reference to British and other European Forms. By Ben Dawes, D.Sc. (London), A.R.C.Sc., D.I.C., F.L.S. [Pp. xvi + 644, with 81 figures.] (Cambridge: at the University Press, 1946. 52*s*. 6*d*. net.)

The need for a recent book in English which covers the whole field of the Trematoda has been felt for years, but the task of the compiler has become such a formidable one, and the knowledge required so extensive, that until now British workers have failed to supply what was one of the most urgent requirements in the whole field of Helminthology. Dr. Dawes's scheme is ambitious and aims at covering not only morphology and taxonomy but life-histories, biology, phylogeny, geographical distribution and history. The mere collection of this information in a single volume will in itself constitute a boon to all workers, and Dr. Dawes should be heartily congratulated on his achievement.

There are some details which are particularly worthy of praise; for example, Table 1 (p. 84), giving the general characters of the main features of the families of the Digenea. The list of popular, as well as scientific names of hosts, is extremely useful. The former are frequently more stable than the latter and their inclusion saves a lot of library work. It is also very satisfactory that at last adequate emphasis is placed on the value of camera lucida drawings. Let us hope all post-graduate students embarking on their first publication will take this chapter well to heart!

There are inevitably some portions of the work which do not reach such a high standard as others. The chapters on the larval forms are notably weak and contain many errors. It is possible that a paragraph has been omitted

between pp. 426 and 427. The Gymnocephalus cercariæ are described as "all poor swimmers . . . living near the bottom of ponds . . . and showing no special behaviour response to light . . . encysting on herbage." Included here is the well-defined group of Opisthorchid cercariæ. These with few exceptions are among the most powerful swimmers of all cercariæ, showing exceptionally clear-cut phototropisms, and encysting in fish! Other types of inaccuracies occur in this section. Thus, for example, on p. 429 it is stated that one species of Cystophorous cercariæ can be added to Miller's (1936) list of fourteen species, whereas in fact at least nine were first described between 1936 and 1941.

The bibliography is extensive and extremely valuable. There are, however, some very curious omissions, among which is the 500-page monograph on Larval Trematodes by Dr. Annie Porter (1938), with descriptions of over 90 new species. Despite the special reference in the title to the British Fauna, some of the relatively important papers of this remarkably scanty literature are not included. But these are details. Dr. Dawes stresses the fact that the book is not intended for specialists, nor is it a text-book. It will prove indispensable and stimulating for students and provide a much needed "take-off" for future research. It will also be invaluable to specialists in other groups who wish to obtain a bird's-eye view of the Trematoda without prolonged and tedious researches in the library.

The Cambridge University Press are to be sincerely congratulated on the high standard of the production.

M. R.

Some Properties and Applications of D.D.T. [Pp. 34.] (London: H.M. Stationery Office, 1946. 6*d*. net.)

In 1942 the ever-expanding needs of the allied armed forces for insecticides to control disease-carrying insects became acute when supplies of pyrethrum and rotenone were cut off by the entry of Japan into the War. The outstanding properties of the synthetic insecticide D.D.T. were announced at a time when the demand was most pressing. A sample was obtained from Switzerland and this proved so promising that an intensive programme of research was put in hand. The work was carried out by various government establishments, by extra-mural teams of workers in the United Kingdom, by various Colonial establishments, service units and by teams of workers from the British Commonwealth and the United States of America. This booklet, issued by the Ministry of Supply, summarises results in this field up to the end of 1945.

The author concentrates on the practical considerations connected with the use of D.D.T.—chemical and physical properties, typical formulations and means of dispersal, as well as toxicity to vertebrates and arthropods. A useful assessment of the control achieved in field trials against a variety of arthropod pests is given in an appendix. The booklet is not a guide to the further literature and indeed is compiled largely from unpublished reports held at the Ministries of Supply and Production. Owing to the delays imposed on publication, it is still difficult to view in perspective the very substantial British contribution to this work.

A. D. L.

Notes on Microscopical Technique for Zoologists. By C. F. A. Pantin, Sc.D., F.R.S. [Pp. viii + 73, with 8 figures.] (Cambridge: at the University Press, 1946. 6s. net.)

The teaching of microscopical technique to students must necessarily follow a somewhat illogical course. Ideally one should begin by explaining the scientific basis of the methods, the physics and chemistry of the processes involved in making the structure of cells and tissues visible. Then one should proceed to an account of the methods themselves, with an attempt at an analysis of those that are empirically developed and improperly understood. In fact, however, the students, as soon as they begin a specialised course in Zoology, will wish to make preparations of the organisms or tissues they are studying, long before they have been able to grasp the principles involved. The value of Dr. Pantin's excellent book is twofold. First, it provides the student with advice as to the best method of demonstrating a variety of the objects he is likely to meet in a zoological course; the selection is based on the author's experience, so that one is saved the embarrassment of choice between the many alternatives offered by standard works such as "Bolles Lee" (the "Mrs. Beeton" of British histology). Second, the book indicates in its rich and up-to-date lists of references how the student can come to understand what he is doing, and how his knowledge of living matter could be extended by the newer methods of microscopy and histochemistry. It is a book that the student will grow out of if he embarks on research work, but it will save him many of the growing pains of his adolescence as a microscopist. W. H.

AGRICULTURE

The Agricultural Development of the Middle East. By B. A. Keen, D.Sc., F.R.S. [Pp. xii + 126, with 15 plates and 2 maps.] (London: H.M. Stationery Office, 1946. 5s. net.)

This report forms part of a survey resulting from the decision of the Middle East Supply Centre to set up a scientific Advisory Mission to examine the principal scientific problems and technical resources, and to make recommendations for their development and for the establishment of the necessary organisation in the Middle East and elsewhere to ensure the practical service of information and advice.

As Dr. Keen, who was entrusted with the agricultural portion of the programme, explains, the Middle East region covers no less than fourteen countries and extends from Cyprus in the north to the Sudan and Ethiopia in the south, and from Tripolitania in the west to Persia in the east. In such a vast region it is only natural that the climatic conditions are extremely diverse, and agricultural development ranges from the most advanced irrigation farming to the ancient pastoral habits of the nomad. It is nevertheless claimed that in spite of these diversities there are many common problems such as the division of the climate into a hot rainless summer and a rainy winter, the predominance of peasant farming and similarity in the systems of land tenure. Although the urgent demands of the War called for an immediate survey, it is believed that it will be necessary to continue to regard these problems on a regional basis after the war, more especially as the organisation envisaged by the Hot Springs Conference will work on a regional basis.

After outlining Middle East Agriculture by territories, the obstacles to agricultural improvement are discussed. The author stresses the difficulties arising from the systems of land tenure and social organisation. In all

countries where agriculture is on a low subsistence level, the greatest difficulties in effecting technical improvements by raising the standard of implements and buildings, or the encouragement of better livestock and seeds, are due to the insecurity of tenure, the indebtedness of the cultivator and the fragmentation of his holdings. The agricultural departments cannot remedy these defects by themselves, their solution requires the whole weight of an enlightened Government. Until some solution is found to these problems, the technical improvements discovered by the research officers of the departments of Agriculture will be difficult, if not impossible, to apply. These obstacles to agricultural improvement are discussed fully and form one of the most valuable sections of the report. As is pointed out, it is simpler to try new systems in areas that are unoccupied or relatively undeveloped. A good example is the Gezira of the Anglo-Egyptian Sudan, where a tripartite partnership between the Government, the tenant cultivators and the Sudan Plantations syndicate has worked wonders. Other efforts on similar lines are the Jewish settlements in Palestine, the Italian settlements in Libya and the Latifiyah Estates in Iraq. The development of the co-operative societies in Cyprus is discussed as a possible avenue for effecting improvements.

Considerable space is devoted to the possibility of effecting technical improvements and the special scientific problems of each territory are briefly outlined.

It is natural that the problems attending the use of organic residues as manures should have been discussed in some detail by the author in view of his researches into soil problems. There will probably be a division of opinion with regard to his advocacy of the peasant's custom of burning animal dung for fuel instead of applying it to the land. Whether the application of farmyard manure to the land in the tropics is a waste of time or whether it does good is at present a matter of controversy, but all will agree with the author that it should be the subject of carefully controlled experiments. What is important to remember, however, is that the peasant will continue to burn dung for fuel until he can get some other source of heat and that the residues with their valuable mineral contents do not go back in the land but usually remain in and around the buildings.

It is good to note that a warning is given against the unrestricted use of tractors; in fact, one could go further and say any mould-board plough, for in the hands of unskilled workers their use may cause untold damage to the land, as experience in Uganda has already shown. Carefully controlled experiment must precede their general adoption.

In the final chapter an attempt is made to suggest methods of effecting improvements. Stress is again laid on the fact that no system of agriculture can be progressive unless the holding can be worked as a unit. One of the difficulties of the small peasant farming system is the difficulty in grading and marketing crops satisfactorily, so that peasant produce has difficulty in competing with plantation goods. To get over this difficulty Dr. Keen has suggested the formation of Public Utility Corporations working with the Government and the tenants. Space does not permit the mention of other important issues raised by the author.

There is an amusing clerical error at the top of p. 63, where the words "peanuts" and "peasant" seem to have become transposed.

The report is accompanied by a series of photographs of topical interest and a folding map. This thoughtful review is well worth the study of all who are interested in agricultural development. G. E.

PHYSIOLOGY AND MEDICINE

Annual Review of Physiology. Vol. VIII. Edited by JAMES MURRAY LUCK. [Pp. viii + 658.] (Stanford University P.O., California: American Physiological Society and Annual Reviews, Inc., 1946. $5.00.)

THIS annual has survived the war, has appeared regularly since 1939, and displays signs of increasing usefulness. The earlier volumes showed a tendency towards the "animated card-index" type of review, but the present series is, almost without exception, critical and readable. The preface indicates that this is in accordance with declared editorial policy. The difficulty of securing foreign journals and the slowness with which work, secret during the war, is now being published are rightly deplored, and the editors might well consider whether any action can be taken to correct this. The reviews have another function besides keeping the current reader up to date; they will be increasingly used as a key to older literature whereby research workers may survey the way in which their particular subject has developed. Contributors for the next few years might be asked to draw attention to any missing work which would have had an important bearing on the reviews of their predecessors. Gaps in the references are inevitable and can be filled from other sources, but apparent jumps in the development of thought on a certain topic should not, if they occur, go unexplained.

The first three reviews treat of general topics—the effects of ultraviolet radiation, aspects of genetics and developmental physiology. Thereafter the main body of the subject is attacked. The sections on heat and cold, the skin, shock, the visceral functions of the nervous system, physiological psychology, and applied physiology all contain information regarding the reaction of the body to stress (particularly temperature change) and, of course, much besides. The influence the war has had upon research is also apparent in the reviews of respiration, aviation physiology and audition. The availability of man for experimental work gains emphasis from the sections on heart and kidneys where we learn that not only can blood be comfortably withdrawn from the heart by venous catheterisation, but that the same technique can be used for obtaining blood from the renal vein. A theme is apparent in many reviews—Pitts shows how the new techniques for testing renal function are displaying the kidney's part in the economy of the body, Gregersen firmly disposes of the general capillary permeability theory of shock, Hare in a well-thought-out contribution stresses the unity of the autonomic system, Dempsey searches for the principles of endocrinology and so forth. Recent work on the digestive system, liver and bile, blood, heart, the somatic nervous system and reproduction is straightforwardly reviewed, and Hooker, in the last-named field, has produced a readable survey which is neither too general nor too limited in its scope. An article by Cope and Rosenfeld suggests that much of interest remains to be discovered about the lymphatic system.

W. H. N.

Vitamins and Hormones. Vol. III. Edited by ROBERT S. HARRIS and KENNETH V. THIMANN. [Pp. xvi + 420, with 18 figures and 64 tables.] (New York: Academic Press, Inc., 1945. $6.50.)

IT is clear from the publication of this volume, the third of the series, that the *Ergebnisse der Vitamin- und Hormonforschung* has not only successfully withstood transplantation from Leipzig to New York, but that its reincarna-

tion under non-Nazi auspices and a new name have resulted in the production of a highly viable organism. Furthermore, a simultaneous change of publisher from the Akademische Verlagsgesellschaft M.B.H. to the Academic Press, Inc., and the editorship from that of Ruzicka and Stepp, and of Mellanby and Ruzicka for Volume II, to that of Harris and Thimann for Volume III, has involved no lowering in standard of the pre-war publication. This, it has to be admitted, was a very high one, in spite of the anti-semitic lunacy that led to the removal of an excellent German editor lest he be contaminated by his association with a volume not unimpeachably "Aryan" in authorship and also made it necessary for the publishers themselves to flee across the Atlantic.

The first volume of *Vitamins and Hormones* was produced in such a way as to make clear to readers that it was, without actually facsimilating the *Ergebnisse*, its linear descendant and would fulfil post-war the functions of the pre-war German publication. It appeared in 1943 and was followed in 1944 by Volume II; the good work has now continued in Volume III. Its international flavour is maintained by a good mixture of British (3), United States (9) and Palestine (2) contributors; further, of the fourteen authors, at least two come from industrial laboratories and the rest from Universities, Medical Schools or Research Institutes. By casting the widest possible net the editors are thus able to secure the services of the best individual experts.

Outstanding in this particular volume is an almost monumental monograph on "Growth Factors in Microbiology" by B. C. J. G. Knight of the Wellcome Physiological Research Laboratories in Beckenham. This review is 110 pages long and furnished with 456 references; it constitutes a thoroughly up-to-date and authoritative survey of what the author himself calls "Some Wider Aspects of Nutritional Studies with Micro-organisms." It deals chapter by chapter with nine substances that are admitted by all or some to fall into the group of water-soluble vitamins, as well as with a number of others, such as glutamine, purines and pyrimidines, oleic acid and naphthoquinones.

Of highly topical interest is the review by Najjar and Barrett of Johns Hopkins Hospital, surveying what is known about the synthesis of B vitamins by intestinal bacteria. Recent investigations in this field and the conclusive evidence to show that a portion, possibly a significantly large portion, of man's aneurine, riboflavine and nicotinic acid intake are derived from the activities of his alimentary allotment, may bring about revolutionary changes in our attitude not only to certain deficiency diseases but also to the relationships between diet and health. The problem of disentangling the extent to which dietary nutrients directly affect the well-being of their consumer and, at the same time, indirectly affect it by modifying his intestinal flora, is a matter that will only be settled by long and patient investigation, and reviews like the present one are of great value in surveying the ground so far covered.

There is no space here to do more than mention in passing the article by T. Moore of the Dunn Nutritional Laboratory at Cambridge, on "The Interrelation of Vitamins," and that by Daft and Sebrell, of the National Institute of Health, Bethesda, on "Sulfonamides and Vitamin Deficiencies"; it may, however, be pointed out that this article dovetails very nicely with that of Najjar and Barrett because certain of the less soluble sulphonamides have been ingeniously used for investigating the difference in nutritive status

of animals with a "normal" alimentary flora and those whose guts have been sterilised with a sulphonamide drug.

Nutritionists will also be interested in Warkany's review on "Manifestations of Prenatal Nutritional Deficiency," contributed from the Children's Hospital Research Foundation of Cincinnati.

In the endocrine field, E. C. Dodds of the Courtauld Institute in London discusses "Possibilities in the Realm of Synthetic Estrogens," while Zondek and Sulman from Jerusalem survey our knowledge of "The Mechanism of Action and Metabolism of Gonadotropic Hormones in the Organism."

Approaching the subject of physiology is the review by D. Nachmansohn from the College of Physicians and Surgeons in New York, concerning itself with "The Role of Acetylcholine in the Mechanism of Nerve Activity."

It is a pity not to be able to give to the 55-page review by SubbaRow, Baird Hastings and Elkin from the Lederle Laboratories on "Chemistry of Anti-Pernicious Anæmia Substances of Liver" as warm a welcome as to the other sections. Little but negative results have point when the substance examined is known not to be completely pure, and this is *a fortiori* truer, the less pure the material investigated. The authors of this article have meticulously surveyed "the progress made since 1926 toward the isolation and identification of the anti-pernicious anæmia material of liver." The passage quoted is immediately followed by the disarming sentence: "Unfortunately, within a short time, save for its historical interest, this review may be without scientific value." Without going as far as this modesty would seem to impel us, it would seem legitimate to question whether elaborate details of methods of fractionation, leading in any event to a relatively "crude" product, can usefully be exhumed from the scientific journals in which they first made their appearance. The authors of this article point out in their final paragraph that the amount of material needed for the patient per day has, as a result of intensive attempts at concentration, decreased from 400 g. to less than 1 mg. It follows, therefore, that the average therapeutic dose cannot be more than 1 mg. Yet the greater part of this review article is concerned with descriptions of the method of preparing concentrates that are only active in far larger doses. In my view, the time is not ripe for surveying the chemistry of this highly important substance. Recent work on folic acid and highly suggestive investigations into the relation between this substance and its conjugates, as well as careful comparison of the effects of such products with those of anti-anæmic concentrates prepared from liver, may well solve the whole problem in a much shorter time than could legitimately have been forecast only a year ago. When that time comes a review by SubbaRow and his colleagues will be most welcome and much more useful than their present gallant but rather ineffective effort.

A. L. BACHARACH.

Food and Health: An Introduction to the Science of Nutrition. By A. BARBARA CALLOW, M.A., M.Sc., M.S. Third edition. [Pp. viii + 184, with 9 figures, including 3 plates.] (Oxford: at the Clarendon Press, 1946. 6*s*. net.)

THIS edition of a very useful book has appeared at a fortunate moment. People need a simple introduction to the science of nutrition and most of such books are out of print. This edition has been almost entirely rewritten and is improved in every respect.

It is an interesting speculation whether it was chance or coincidence that gave Mrs. Callow her initials, still unchanged when she married. Anyhow she has given us in this book the A B C of nutrition in a very clear and logical way. It is difficult, for example, to see how the explanation of that stumbling-block to the layman, the biological value of proteins, could be bettered. The compilation on p. 6 of the nutritive value of some proteins will be hailed with delight by teachers of the subject, though not, we think, by all vegetarians. As scientist, perforce turned housewife, Mrs. Callow has the practical application of the science of nutrition not only in mind but in hand, and makes many common-sense suggestions about the choice of food and everyday meals in the later pages of her book.

One mild grumble may be allowed. Mrs. Callow still retains family coefficients in dietary surveys, though she warns us that though they "are correct for calories they cannot be correct for all other nutrients." Why mention them, then? They may mislead lay folk, for they have been known to mislead nutritionists. Most of us can see little difference between 3000 + 2400 + 1800 + 1500 and 3000 (1 + 0·8 + 0·6 + 0·5). The latter *looks* more mathematical, that is all. But this is a small matter in a book which can be recommended to the general reader for its clarity, simplicity of style, common sense and logic.

V. H. M.

Chemotherapy, Yesterday, To-day, and To-morrow. By SIR ALEXANDER FLEMING, M.B., F.R.C.S., F.R.C.P., F.R.S. [Pp. 39, with 2 plates and 5 figures.] (Cambridge: at the University Press, 1946. 2*s*. net.)

THIS is a clearly written authoritative account of the control of bacterial infections by chemical substances. The author traces the development of chemotherapeutics from Lister's use of carbolic acid as an antiseptic, through the large number of chemicals introduced unsuccessfully for the treatment of localised infection, to the extensive employment of Dakin's fluid for septic wounds in the 1914–18 war.

Ehrlich's Salvarsan was the first real success in this form of treatment for bacterial diseases, and, although it proved to be less efficient than was originally hoped, it stimulated research on chemotherapeutic drugs.

In 1935 Domagk showed that Prontosil had a curative action on mice infected with streptococci, and within a few years many closely related sulphonamide drugs had been discovered with therapeutic effects on certain bacterial infections.

The last chapter of the story, at present, is the discovery and use of penicillin, in which Sir Alexander Fleming has taken such a prominent part, and gramicidin, which would probably have been more widely used had not penicillin been completely non-toxic. The author is certain that other antibiotics will be discovered. Already streptomycin has been produced, and many teams of investigators are seeking more useful and more powerful substances.

Any person requiring a non-biased and accurate account of this fascinating branch of medicine will find this booklet, based on the Linacre Lecture 1946, interesting and extremely readable.

T. C.

MISCELLANEOUS

The Outlook of Science: Modern Materialism. By R. L. Worrall, M.B., Ch.M. Second edition. [Pp. 191.] (London, New York, Toronto: Staples Press, Ltd., 1946. 12*s*. 6*d*. net.)

This book, the first edition of which was published in 1933, is a highly polemical exposition of the standpoint of dialectical materialism which was brought into prominence by Marx, Engels and Lenin, and developed by recent Soviet writers such as Zavadovsky. Dr. Worrall evidently considers attack the best form of defence and criticises with great vigour all forms of idealistic doctrine, from Berkeley to J. S. Haldane and the modern physicists who dabble in philosophy. But the mechanists also come under his condemnation: Hogben, J. B. Watson and his behaviourism, and even Pavlov in his neglect of mind, are subjected to criticism. Dialectical or "modern" materialism is not mechanistic in the old sense. What then is it? The book does not make this entirely clear, and it is a pity Dr. Worrall did not give more space to exposition and less to criticism of opposing views. The main principles are summarised as follows: "The universe is matter in various forms of motion. . . . Matter is self-motivated and everywhere continuous in the dynamic relations of its different structural forms. Physical change is the sum total of various forms of motion, integrated in an infinite variety of events and processes. Physical change occurs through the developing unity of opposite and interpenetrating qualities. Quantitative changes give rise to qualitative changes, and vice versa. Thought is a function of the brain, which is matter organised in the course of evolution as a highly complex structure of nerve cells. Mind reflects in perception the independently existing reality of the ever changing physical world" (p. 10). The point of view is realistic and dynamic, and curiously reminiscent of the poetic and naïve materialism of Lucretius. But "modern materialists" see in matter much more than inert particles in motion. "The evolution of living matter," writes Dr. Worrall, "and the astounding facts of recent embryology are fundamentally incomprehensible without a recognition that matter is self-motivated. 'Inert matter moved by a non-material energy' is a hopelessly inadequate concept for a rational and comprehensive interpretation of biological phenomena" (p. 178). One begins to wonder why they call themselves materialists; realists, yes, since they consider reality to be independent of mind, but their conception of "matter" and its potentialities goes far beyond what is commonly understood by the term.

E. S. R.

BOOKS RECEIVED

(Publishers are requested to notify prices.)

Legendre Polynomials. Mathematical Tables Part-Volume A. British Association for the Advancement of Science. Prepared by the Committee for the Calculation of Mathematical Tables. Cambridge: at the University Press, 1946. (Pp. 42.) 8*s*. 6*d*.

The Airy Integral, giving Tables of Solutions of the Differential Equation $y'' = xy$. Mathematical Tables Part-Volume B. British Association for the Advancement of Science. Prepared by J. C. P. Miller on behalf of the Committee for the Calculation of Mathematical Tables. Cambridge: at the University Press, 1946. (Pp. 56.) 10*s*. (Auxiliary Tables, I: Coefficients in the Modified Everett Interpolation Formula; II: Tables for Interpolation with Reduced Derivatives. Coefficients for Function and for First Derivative. 6*d*. each.)

Les Principes du Calcul infinitesimal. Par René Guénon. Paris: Librairie Gallimard, 1946. (Pp. 141.)

The Advanced Theory of Statistics. Vol. II. By Maurice G. Kendall, M.A., an Hon. Secretary of the Royal Statistical Society, Statistician to the Chamber of Shipping of the United Kingdom. London: Charles Griffin & Co., Ltd., 1946. (Pp. viii + 521, with 30 figures and 52 tables.) 50*s*. net.

A Manual of Operation for the Automatic Sequence Controlled Calculator. By the Staff of the Computation Laboratory. Cambridge, Mass.: Harvard University Press; London: Oxford University Press, 1946. (Pp. xiv + 561, with 17 plates and 44 figures.) 56*s*. net.

La Mécanique ondulatoire des Systèmes de Corpuscules. Par Louis de Broglie, Membre de l'Institut, Professeur à la Faculté des Sciences de Paris. Collection de Physique Mathematique, Fasc. V. Paris: Gauthier-Villars, 1939. (Pp. vi + 223, with 19 figures.) Frs. 250.—.

Photometric Atlas of Stellar Spectra. By W. A. Hiltner and Robley C. Williams. Book I: Spectrographic Data and Dispersion Tables; Book II: Alpha Bootis K2 pec. Tracings from Lambda 3982 to Lambda 6723; Book III: Alpha Cygni A2 Ia. Tracings from Lambda 3993 to Lambda 6620; Book IV: Beta Orionis B8 Ia. Tracings from Lambda 3916 to Lambda 5982; Book V: Alpha Lyrae A0 V. Tracings from Lambda 3925 to Lambda 5908; Book VI: Alpha Canis Majoris A1 V. Tracings from Lambda 3916 to Lambda 6302; Book VII: Alpha Canis Minoris F5 IV. Tracings from Lambda 3988 to Lambda 6187; Book VIII: Alpha Persei F5 Ib. Tracings from Lambda 3988 to Lambda 6688; Book IX: Alpha Orionis M2 Ib. Tracings from Lambda 4065 to Lambda 6627. Ann Arbor: University of Michigan Press; London: Oxford University Press, 1946. 42*s*. net.

Earth, Moon and Planets. By Fred L. Whipple. The Harvard Books on Astronomy. London: J. & A. Churchill, Ltd., 1946. (Pp. viii + 293, with frontispiece, 140 figures and 1 folding plate.) 18*s*. net.

The Milky Way. By Bart J. Bok and Priscilla F. Bok. Second edition. The Harvard Books on Astronomy. London: J. & A. Churchill, Ltd., 1946. (Pp. vi + 224, with frontispiece, 100 figures and 2 folding plates.) 18*s*. net.

Telescopes and Accessories. By George Z. Dimitroff and James G. Baker. The Harvard Books on Astronomy. London: J. & A. Churchill, Ltd., 1946. (Pp. vi + 309, with frontispiece and 146 figures.) 18*s*. net.

Frontiers of Astronomy. By David S. Evans, M.A., Ph.D., F.Inst.P. Sigma Introduction to Science 1. London: Sigma Books, Ltd., 1946. (Pp. 175, with 8 plates and 47 figures.) 6*s*. net.

I Predict a Storm. By P. H. Jones, Christchurch, N.Z. (Pp. 79, with 48 figures.) 7*s*. 6*d*. net.

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SCIENCE PROGRESS

THE LATE-GLACIAL PERIOD

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At the maximum glaciation of the last Ice Age, the ice-front reached Jutland, Holstein, and East Prussia, and between it and the northwards extension of the Alpine ice-fields a belt of land in places no wider than 500 km. or so was left. Over much of this country a so-called peri-glacial climate prevailed, recognisable by frost-modified soils (*Cryoturbatic* phenomena of Florschütz, or *Congeliturbation* of Bryan). Wind-borne dust was deposited as loess over considerable areas; ocean-level was lower than it now is by some hundreds of feet, so that the British Isles were part of the Continental land-mass. In the British Islands also ice-sheets covered a substantial part of the country and we may assume peri-glacial climate for much of the rest.

The extreme conditions of this time make it an appropriate basis from which to regard the history of the physiography, fauna, flora, and human occupation as they progressively approach their present-day status. The period of time thus embraced is of the order of 18,000 years, and embraces the two great periods of the late-glacial and the post-glacial. It was until recently customary to define the end of the late-glacial period as coinciding with the bi-partition of the Swedish ice-sheet at Ragunda, which, however, is now known to be as late as the *Ancylus* period, that is, within the post-glacial warm period. The last few years have seen the view accepted that the end of the late-glacial period should be set at the time when a cover of woodland first extensively replaced tundra-vegetation in southern Scandinavia, Denmark, and northern Germany. This appears to correspond with the phase, which began about 8500 B.C., of glacial retreat from the great line of end-moraines which cross southern Sweden and which are contemporaneous with the Finnish Salpausselkä moraines. It is now recognised that there was then no regular recession of a continuous ice-front to central Sweden, but melting was rapid and general and left discontinuous

masses of dead ice everywhere, whilst open birch-pine woods rapidly colonised the region thus made free.

The deposits of lakes and bogs, investigated by the technique of pollen-analysis, have presented a substantial picture of vegetational history of much of Europe from this time forward, that is, for post-glacial time. The history of replacement of birch-pine forests by the warmth-demanding trees is now a familiar one, and it is known how throughout western Europe this replacement phase coincided with a phase of a remarkable preponderance of hazel pollen. There ensued in the post-glacial climatic optimum dominance of the mixed oak forest and optimal extension of warmth-demanding species of plants and animals. Later, in the last 2500 years climatic deterioration has been accompanied by a partial reversion of forest-history.

Whilst knowledge of the post-glacial period thus advanced rapidly, relative obscurity at first prevailed over the preceding period, the late-glacial. Work published during the last ten or fifteen years, however, gives promise of swift elucidation, and this turns upon two or three particular features. Firstly, the recognition that the course of climatic amelioration in the late-glacial was everywhere interrupted by a temporary setback, so that a somewhat warm interstadial phase was succeeded by returning conditions of coldness before the resumption of the general amelioration. From the Zealand site, where deposits of this phase were first described, this is referred to as the Allerød phase; it has now been widely encountered and clearly affords a means of recognising, and at the same time sub-dividing, late-glacial deposits over much of north-western Europe.

In the second place the technique of pollen-analysis, which at first was exploited exclusively to determine the forest vegetational sequences, has been improved and extended to permit the recognition of pollen of a considerable range of plant species beyond those of the forest dominants. The contemporary rise of pollen investigations in relation to hay-fever has assisted this process, and now analysis of the "non-arboreal pollen" (N.A.P.) alongside the "arboreal pollen" (A.P.) is becoming of great value. Firbas pointed out at an early stage the value of the N.A.P./A.P. ratio as an index to the treelessness or afforestation of a region, and it is now generally found that the opening of the post-glacial period can be detected by the rapid fall in the values of the ratio at this time. In contrast to the possible expectation of heath-clad wastes, the non-tree pollen, consisting overwhelmingly of grass and sedge pollen, pointed to grass-sedge tundra.

Pollen-analysis of course tends to give a *general* picture of vegetational composition, grains are often carried for long distances by the wind or by water before final incorporation, and pollen derived from older beds may easily be incorporated in newly-forming deposits. For these reasons their study is naturally supplemented by extraction and identification of macroscopic fossils, such as flowers, leaves, wood, fruits, and seeds, which are likely to be of more local origin and also to permit specific diagnosis.

The stratigraphic evidence of the Allerød oscillation is of considerable interest. As described by Hartz and Milthers at Allerød itself, there is a deep-basin in which 3 or 4 m. of peat overlies strongly laminated clay up to 5 or 6 m. thick and containing sandy layers with plant remains and also pebbles of chalk and of clay. The clay is divided, some 1½ or 2 m. from its base, by a layer of organic lake-mud (nekron-mud), up to 30 cm. in thickness. The evidence of the plant remains indicates that the lake mud was formed under temperate conditions, whilst the clays above and below were formed under an arctic climate. The upper clay was not brought in by downwash, but by a solifluction process. *Betula nana* (the arctic birch) and *Dryas octopetala* were recovered from the sand layer in the clay, and remains of the large-leaved (tree) birches were found in the nekron-mud.

A similar threefold division to this has been encountered since in many sites in Denmark, Sweden, Germany, and Ireland. In England it appears to be represented at the Hawke's Tor China Clay Pits on Bodmin Moor, Cornwall, where unpublished work on the pollen by Mrs. E. M. Megaw and on other plant remains by Miss A. P. Conolly support this interpretation. The sequence of older Dryas clay—lake-muds—younger Dryas clay is now become familiar in middle and western Europe, and corresponds with the pollen-zones I, II, and III, in use by Jessen for Denmark and Ireland.

Hartz, shortly after publication of results at the type site, described a second type of Allerød stratigraphy. At Femsølyng there was a thin layer of lake-mud containing tree-birch (clearly the Allerød mild phase), overlaid by Dryas clay. Beneath the lake-mud, however, instead of Dryas clay were a few cm. of sandy, dark mould with fine leaves, twigs, and roots of tree-birches, large willows, Arctostaphylos, etc., and in one place a large birch tree was found rooted in the moraine-clay beneath. Hartz explains that the basin did not exist in Early Dryas time, but that its site was occupied by a large embedded mass of "dead" ice. In the mild Allerød period the ice-block melted so that the floor of the

birch-willow wood growing on the moraine clay became submerged in the lake thus created. This land-facies of the Allerød period has been found elsewhere, naturally associated with the kettle-holes made by the melting of buried ice. Possibly the steep-sided lake basin described by Hardy from Whattall Moss, Shropshire, is of this nature. A third type, a deep-lake facies, has been described from Windermere in the English lake-district by Pennington, who had the advantage of using the Jenkin sampler which will take undisturbed cores from beneath deep water. The late-glacial layers are here pink and grey clays exhibiting fine laminations, probably annual varves, interrupted by a grey-brown organic lake-mud a few centimetres in thickness, which represents the milder Allerød phase when organic growth in the lake was possible and when the surrounding ground, now clad with vegetation, yielded less mineral matter to the streams feeding the lake.

In yet other types of terrain other facies of the Allerød sequence probably remain to be described, and it seems probable that in shallow lakes of gently rolling country stratigraphic evidence for the climatic oscillation may be poor.

The nature of the evidence that the Allerød period had a favourable climate can be gathered by the points quoted by Schütrumpf from the Holstein investigations. They are:

(1) Colonisation of the lake, and sedge-peat formation,
(2) Increased thawing of dead ice, and the sinking of peat above it,
(3) Recession of the non-tree pollen,
(4) High values for pine-pollen, together with cones and stomata,
(5) Decrease and lack of Selaginella spores, and pollen of Empetrum and other ericoid plants, all of which are presumably shaded out by tree growth,
(6) Absence of *Betula nana*, which is abundant above and below and which also needs open conditions.

Evidence that the climate afterwards worsened is summarised by Schütrumpf as lying in:

(1) Rise in the non-tree pollen,
(2) Recurrence of dwarf birch instead of tree birches,
(3) Rise of the birch pollen-curve at the expense of that of pine,
(4) Rise of willow pollen to values of 15–20 per cent.,
(5) Return of Selaginella, Empetrum, and the Ericaceæ,
(6) Return of pollen of the sea-buckthorn (*Hippophæ rhamnoides*).

A sufficiently large number of sites have now been investigated for Schütrumpf to complete an outline diagram illustrative of

vegetation conditions in the Allerød period, and from this and the summaries of Firbas, Gross, Gams, and Jessen, it appears that over southern Sweden, Norway, most of Denmark, and Ireland, thêre existed a grass-sedge tundra with scattered patches of tree-birches; what Gross speaks of as "open sub-arctic wood with hypnum-moss mire". In Holstein and other parts of Northern Germany the vegetation was apparently, to begin with, closed woods of tree-birch, and later woods of pine; remains of aspen have also been found. In the extreme north-west of Ireland Jessen reports such consistently high values of pollen of *Empetrum* as to suggest the presence of *Empetrum* heath.

The tundra vegetation of the periods preceding and following this mild stage included, besides the grasses and sedges so strongly indicated by the pollen-diagrams, very abundant dwarf birch and willow, the arctic *Dryas*, *Oxyria*, *Armeria*, *Empetrum*, and *Selaginella*. In addition, many unexpected plants are indicated abundantly by their pollen: these include the genera *Artemisia*, *Rumex*, *Thalictrum*, *Hippophæ*, and *Helianthemum*. Perhaps the least expected of these is the *Artemisia*. These facts have suggested to Iversen affinities with central-European alpine vegetation rather than with arctic or sub-arctic vegetation of to-day, and he proposes the introduction of the term "park tundra"—"for the curious open country that spread over immense regions at the close of the glacial age, and with its mixture of grasslands and tree-islands provided ideal living conditions for the rich late-glacial fauna".

The evidence for fauna here mentioned is now of considerable extent. Iversen has related finds of bison (*Bison bonasus arbustotundrarum* and *B. b. priscius*) to the close of the late-glacial period and has shown its immediate disappearance in the following forest period. Similarly in Ireland Jessen and Mitchell have shown that remains of the Giant Irish Deer (*Cervus megaceros*) are very closely associated with lake-muds of the Allerød period but are absent from post-glacial layers. With the bison in Denmark were other large mammals, the wild horse, elk, and reindeer, and the latter animal was abundant also in the Irish late-glacial deposits. Mitchell has suggested, with reservations, the possibility that the mammoth may have survived in Ireland at this time. A recent discovery of a skeleton of the elk (*Alces alces*) at Neasham, near Darlington, appears also to come from late-glacial beds. It seems evident that the open tundra conditions favoured these animals and that their extinction coincided with expansion of the forests. As would be expected, suitable sites have yielded evidence of many

smaller animals, including some of arctic or "steppe" affinities; such are wolf, fox, hare, lynx, lemming, marten, beaver, ground-squirrel, mouse-hare, and ptarmigan.

Nowhere have conditions of the late-glacial period been more thoroughly investigated than in the great excavations carried out under the direction of Rust at Meiendorf and Stellmoor in Holstein. The infilling of an extinct sub-glacial valley discloses the full sequence of geological events, and archæological events are correlated with them by the fortunate chance that prehistoric man so consistently chose to live on the bank of the channel that artifacts of three separate periods are stratified into the deposits. The two oldest series appear to represent the summer camps of reindeer-hunters, for not only are the artifacts associated with great numbers of the bones and antlers of reindeer, but there are present partly worked pieces of this material in such profusion that the methods of tool construction can easily be recognised. The oldest culture is the so-called Hamburgian already described by Schwantes from surface finds, of upper Palæolithic affinities: this lies in the lowest deposits of the channel in the Tundra period of Zone I. The second culture is the Ahrensburg, which falls approximately within the milder period of Zone II, the Allerød proper, and which corresponds with the previously known "Lyngby" culture. Indeed numbers of the type artifact, the reindeer antler "Lyngby axe," were discovered *in situ*. This dating agrees with that suggested by Iversen from his pollen-analysis investigations at the type site in Jutland, and to the same period belong the bone point of elk bone from Gumbinnen and the bone dagger from Abschruten, both placed at this horizon by the East Prussian investigations of Gross. It should be noted that the wooded character of the Holstein country in the Allerød period is associated with various wooden objects such as pine-wood arrowshafts. Finally at the highest level in the deposits at Duvensee the Maglemosean culture is encountered, a mesolithic culture already familiar in western Europe and dated elsewhere, as here, to the Boreal period of the first expansion of warmth-demanding forest-trees. This correlation between climate, stratigraphy, vegetation, fauna, and prehistoric cultures is a remarkable achievement, only matched to a partial extent in other sites. Thus far the British Isles have yielded no archæological correlations with late-glacial deposits of the character we are describing.

A point of further interest appears to be emerging from continental studies of the late-glacial period, in the apparent recognition of a double character of the Allerød warm period, or, perhaps more

probably, in an earlier and less pronounced interstadial than that now spoken of as the Allerød. This phenomenon was described by Iversen from Jutland as the "Bølling-oscillation" and by Faegri from south-west Norway as the "Brøndmyr-interstadial": Gross has described similar effects from East Prussia. Further evidence is needed of this phase, and traces of it should be sought in this country.

Within the British Isles our knowledge of late-glacial phenomena is much further advanced for Ireland than elsewhere, owing to the very considerable researches of Professor Knud Jessen, of Copenhagen, and Mr. F. Mitchell, of Dublin, and their colleagues on the Irish Committee for Quaternary Research. Dr. Jessen published with Dr. Farrington in 1938 the results of their most interesting late-glacial investigations at Ballybetagh and at Ralaghan, but a much greater volume of Jessen's results is due for publication shortly; some indication of its wide scope and importance was given at the recent meeting of the British Ecological Society held in London on October 15, 1946, when survival and extension of flora and fauna in glacial and post-glacial times were discussed in the light of Quaternary historical investigations.

A point strongly made at this meeting was the need for equating the late-glacial phases, especially the Allerød oscillation, with the known glacial geological phenomena of various parts of Britain. Farrington has already shown that at Ballybetagh the solifluction period of Zone III corresponds with the Wicklow Mountain glaciation after the deposit of the newer drift; it so far appears that the Allerød deposits are absent from Northern Ireland, and the questions are raised of how far Zone III corresponds also to the Scottish readvance stage, and whether we may not find indications of a local Welsh glaciation also at this time. With this is bound up the question of the relative movements of land and sea-level which so much effect the possibilities both of survival and of immigration of fauna and flora. There can be no doubt that here lies an extremely promising field of investigation. Situated between Ireland and the north-western continent, the evidence from Great Britain will be essential to any integrated concept of late-glacial conditions in western Europe and the methods and promise of collecting it should now be apparent.

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THE SOURCE OF STELLAR ENERGY

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EARLIER HYPOTHESES

THE origin of the vast outpouring of radiant energy from the stars has long been one of the most fundamental and challenging problems of astronomy, or indeed of science, since the existence of life on the earth is so completely dependent upon the solar radiation. Although it is believed that this problem is now solved, it is perhaps worth while to survey briefly some of the more plausible hypotheses previously advanced. In so doing we may arrive at a clearer appreciation of its nature and magnitude and of the difficulties involved in its solution.

It is natural to consider the sun in the first instance, not only because of our special interest in its behaviour, but also because of our exceptionally detailed knowledge of its characteristics. Since it is not far from the average in size, mass and luminosity, it is likely that any general conclusions reached will apply to the majority of stars also. Further, if a satisfactory mechanism for the maintenance of the sun's radiation is established, we may reasonably expect that it will only need modification in detail, and not in principle, in order to account for associated, although extreme, stellar types such as blue giants and red dwarfs. Whilst it may not provide a complete explanation of exceptional stellar phenomena such as white dwarfs and novæ, it is likely to throw valuable light on such problems.

The total emission of radiation from the sun may be expressed in various ways. In ordinary engineering units it amounts to about 4×10^{23} kilowatts, or about 6 kw. per sq. cm. (*i.e.* 52 HP per sq. in.) of surface. Since, however, the generation of this radiant energy, by whatever mechanism, cannot be confined to the surface, but must be distributed through the interior, or some part of it, it is better to consider the power emitted per unit volume rather than that per unit area. It also leads to a figure of convenient size, namely, 1·9 ergs per gram per sec. This may seem somewhat small, until it is remembered that, in order to obtain the total emission since the formation of the sun, it must be multiplied by the age of the sun in seconds (say, $6{\cdot}3 \times 10^{16}$, *i.e.* 2000 million years), which gives $1{\cdot}2 \times 10^{17}$ ergs per gm. Even without anticipating any favours still to come, this figure disposes at once of two of the

simplest hypotheses which could be advanced. One is that the radiation is derived from a store of original heat, but this would require either an enormously high initial temperature, of the order of 10^9 ° C., or a very large increase of specific heat with temperature, both of which suppositions may readily be shown to be untenable. The other is that chemical combination, *i.e.* combustion, might be responsible, but this again is out of the question not only because the energy involved is far beyond that liberated by any known or conceivable chemical reaction, but also because chemical combination could not take place at the temperatures prevailing in even the outermost layers of the sun; even if it could there would be no means of disposing of the products of combustion.

Two other hypotheses, both depending upon the conversion of mechanical energy into heat, were put forward about the middle of the nineteenth century. Mayer suggested that the solar radiation might be maintained by meteoritic bombardment, but it was found that this demanded a concentration of matter in the neighbourhood of the sun which was quite incompatible with the unperturbed motion of comets in this region. The earth also would sweep up meteorites at a rate which would produce a continuous and considerable temperature rise, and the increase of the sun's mass would be inadmissibly rapid (double in about 30 million years). Helmholtz's hypothesis, subsequently developed by Kelvin, attributed the generation of heat to the potential energy liberated by the gradual contraction of the sun. A decrease in diameter of some 250 feet per annum would suffice, and this would only be detectable by direct measurement over a period of many thousands of years. A serious difficulty was encountered, however, when the process was extrapolated backwards in time to the point at which the sun's diameter equalled that of the present orbit of the earth. This would clearly set an upper limit to the age of the earth, and the result obtained by Kelvin, namely 20 million years, was much less than that demanded by geological evidence, which at that time could not accept an estimate of less than 100 million years. Two points may be noted here. First, the geological estimate is now known to have been very conservative, and has been raised, mainly on the basis of the concentration of radio-active products in the earth's crust, to something between two and three thousand million years. Second, Kelvin was careful to qualify his conclusion with a reference to the possibility of the existence of sources of energy then unknown to science.

There the matter rested for some fifty years, when the discovery of radioactivity appeared to offer a prospect of escape from the

dilemma. Radium itself, for example, generates heat at the rate of $1 \cdot 6 \times 10^6$ ergs per sec. per gm., but its half-life is only 1600 years and it cannot therefore make any appreciable contribution. On the other hand, uranium, although possessing a suitable half-life ($4 \cdot 4 \times 10^9$ years) generates only 1 erg per sec. per gm., so that even if the sun consisted entirely of uranium its emission would still be only half of that actually observed. There is, in fact, no evidence for the presence of uranium in the sun, and it is unlikely that there can be much. None of the other radio-active elements fulfils the threefold requirement of suitable stability, rate of emission and abundance, so that they cannot provide the source we seek. But it is significant that the radio-active atomic nuclei are capable of generating quantities of heat which are of the right order of magnitude in relation to the mass concerned. Thus, for example, 1 gm. of radium in decaying completely would emit about $1 \cdot 5 \times 10^{17}$ ergs (*cf.* $1 \cdot 2 \times 10^{17}$ emitted per gram of sun in 2000 million years). According to Einstein's theory of the equivalence of energy and mass ($E = mc^2$) this corresponds to only a small fraction (1/6000) of the original mass, and we are thus led to the hypothesis that stellar radiation may be derived from the transformation of matter into energy. The ratio of exchange is so favourable, and the resulting loss of mass so small, that there will be no difficulty in accounting for the immense quantity of energy radiated. The problem becomes one of finding a sub-atomic reaction which will proceed at such a rate, under the conditions obtaining in stellar interiors, as to produce the emission actually observed. The solution of this problem requires quantitative knowledge of the physical and chemical state of the interior of a star, together with comprehensive data concerning all those nuclear reactions which could possibly occur in these circumstances. The former we owe largely to the theoretical work of Eddington; the latter to a number of experimental workers, of whom Rutherford was the first. The combination of the two is due primarily to Bethe. Having regard to the difference in scale of the two sets of phenomena, and to the significance of the results, the achievement must be regarded as one of the most striking in the history of science.

The Internal Constitution of the Stars

The primary physical quantities determining the condition of the interior of a star are temperature, pressure and density. In order that the surface emission may be maintained there must be an inward temperature gradient and therefore a very high temperature at the centre. The pressure also must, on account of gravita-

tion, increase steadily towards the centre up to a very high value, although it may be to some extent reduced by radiation pressure, which has an outward resultant due to the direction of the temperature gradient. The density depends upon pressure, temperature and composition. It must be greater in the interior than at the surface, but cannot be of a different order from the average, which is seldom much greater than unity. The question of composition is in a sense more physical than chemical, since under the enormous pressures obtaining in the central region the atomic electron shells are crushed or stripped off, leaving the nuclei bare. A nucleus of mass A and charge Z will in these circumstances contribute Z free electrons, and the average mass of the separate particles (including the nucleus) will be $A/(Z + 1)$ atomic units. The extreme range of this quantity is only from 0·5, for hydrogen, to 2·6 for uranium, so that the question of chemical composition is relatively unimportant, especially if, as is commonly the case, there is evidence that hydrogen and helium are the main constituents and that considerable quantities of heavy elements cannot be present.

In the case of the sun, the values accepted at present for the central region are a temperature of 20 million degrees C., a pressure of 10,000 million atmospheres, and a density of about 80 grams per c.c. All of these values decrease rapidly with increasing distance from the centre. Valuable additional information bearing on our problem can be obtained by taking other stars into consideration, and especially those which, together with the sun, make up the so-called " main sequence." It was first found by H. N. Russell that the luminosities and temperature of the majority of stars for which reliable values were available exhibited a marked correlation, strongly suggesting that they formed an evolutionary sequence. Similar correlations were later found to hold between these quantities and masses and radii as well. It then became possible to estimate on the basis of Eddington's theory, the central temperatures and the average rates of emission of energy per unit mass. The remarkable result emerged that over the extreme range of masses, *i.e.* from 1/10 to 17 times that of the sun, the central temperature only increases by a factor of about 2, *i.e.* from 14 to 32 million degrees, whereas the energy emission increases by a factor of some 360,000, *i.e.* from 0·01 to 3600 ergs per gm. per sec. If a power law is assumed, this implies that the emission varies as T^{15}. This result is of course only approximate; comparison between the hottest stars and the sun, for example, leads to T^{16}, but the exponent can hardly be in error by more than a few units, and we may therefore rule out any proposed mechanism of energy production which does not possess

a temperature coefficient of this order. In fact, no known physical processes are capable of satisfying such a requirement except certain nuclear reactions, and quantitative application of the criterion enables us to eliminate the majority of these immediately.

Nuclear Reactions

The essential pre-requisite for the occurrence of a nuclear reaction is a collision of two nuclei with a sufficiently large relative velocity. There is no precisely definable value of this, as there is, for example, in the case of the dissociation of a molecule by the impact of an electron. There is instead a definite probability of its occurrence for any given velocity, which can be expressed as a function of the velocity provided that the energy changes involved are known. In the case we are considering, and indeed in all naturally occurring reactions, except for a few special instances, the velocities depend solely upon the temperature, and the probability of a nuclear reaction may therefore be expressed as a function of temperature. In the case of the heavier nuclei the temperatures required to sustain an appreciable reaction rate are far above those calculated by Eddington's theory for stellar interiors. This is due to the relatively large electrostatic field associated with a nucleus of high atomic number. It is true that neutrons of low velocity may induce exothermic transformations of heavy nuclei, but there is no known means by which neutrons could be produced in the type of star under consideration. In any case, the heavier elements occur in only small proportions in stellar atmospheres, and there is no evidence to suggest that their concentration is much greater at deeper levels.

It is natural therefore to examine in the first place reactions between light nuclei. A large number of these are known, but the conditions which they must satisfy in order to qualify for consideration are so stringent that the search is a much less arduous undertaking than might have been expected. Bethe, in a comprehensive examination of all known and certain hypothetical reactions, has shown that only collisions of protons ($_1H^1$) with other nuclei need be taken into account, and that the majority of these must be ruled out because of the rapid consumption of the reactants. That is to say, although such reactions may have contributed at lower temperatures, the supply would have been exhausted long before a temperature of 2×10^7 degrees had been attained. This applies, for example, to the nuclei of Li, Be and B, and it is probably significant in this connection that there is a marked deficiency in the abundance of Li, Be and B, relative to the neighbouring elements H, He, and C, N, O, not only in the earth's crust but also in meteorites

and in stellar atmospheres. There is evidence, as we shall see later, that these elements are concerned in the evolution of energy in certain classes of stars, but these are much cooler than the sun.

There is in fact only one type of nucleus, namely hydrogen, the concentration of which ($\sim$ 35 per cent.) is sufficient to warrant its consideration as a possible solar fuel. The concentration of helium, estimated by Schwarzschild at 40 per cent., would be sufficient were suitable reactions possible, but they are not. The helium nucleus, it appears, is as inert in this sense as the helium atom is in the ordinary chemical sense.

Let us consider first, then, the reaction between two hydrogen nuclei, or protons. This results in the formation of a deuteron (D, or ${}_1H^2$) and the emission of a positive electron, according to the equation ${}_1H^1 + {}_1H^1 = {}_1H^2 + e^+$. Bethe and Critchfield have calculated that this process would give an energy evolution of about 2·2 ergs per gm. per sec. in the conditions obtaining at the centre of the sun. It would be followed by a proton-deuteron reaction resulting in the formation of a He nucleus of mass 3 and the emission of radiation, thus: ${}_1H^1 + {}_1H^2 = {}_2He^3 + \gamma$. This in turn is succeeded by a chain of reactions involving the capture of another proton, which leads to the formation of a normal helium nucleus ${}_2He^4$. It is found, however, that the total rate of energy generation is only increased in consequence by a small fraction, say to about 2·5 ergs per gm. per sec. This is certainly of the right order and it could be maintained for an adequate time, but it is clearly insufficient in view of the fact that the reaction rate falls off rapidly with temperature, *i.e.* as the distance from the centre increases, and the average rate for the whole of the sun would therefore fall far below the required value of about 2 ergs per gm. per sec. Bethe and Critchfield conclude that this process of helium building from protons via deuteron formation makes an appreciable but not the chief contribution to the maintenance of the sun's temperature, although for less massive and cooler stars it may well be the principal source. Moreover, its temperature coefficient ($\sim T^{3\cdot5}$) is so much below that characterising the main sequence as a whole ($\sim T^{16}$) that it could not possibly be of importance except for the coolest stars of the sequence.

Nevertheless, the formation by some means of helium nuclei from protons appears to be the only process which offers any possibility of a solution of our problem. Since no other building-up process but the one described above can possibly occur, we are bound to look for one of an indirect character, involving disintegration of heavier nuclei. The difficulty in this is the relatively low

abundance of such nuclei, which would seem to limit seriously the duration of any such process, if it involves their continuous destruction without replacement. The difficulty could be evaded ; in fact could only be evaded if the heavier nuclei concerned in the series of reactions were reformed as fast as they were destroyed, that is to say if they behaved as catalysts, in the accepted chemical sense. This reasoning may appear obvious at the present time, but full credit must be given to Bethe for its successful application to the discovery of a chain reaction of this type which fulfils all the necessary conditions.

The nucleus which plays the part of catalyst is ${}_6C^{12}$. After four successive reactions with protons, involving the formation of various carbon, nitrogen and oxygen nuclei, a helium nucleus and a ${}_6C^{12}$ nucleus are produced. The process is thus cyclic and can be repeated indefinitely so long as an adequate supply of protons is available, and other conditions remain favourable. The reactions are as follows:

$$
\begin{aligned}
&{}_1H^1 + {}_6C^{12} = {}_7N^{13} + \gamma\,; \quad {}_7N^{13} = {}_6C^{13} + e^+\\
&{}_1H^1 + {}_6C^{13} = {}_7N^{14} + \gamma\\
&{}_1H^1 + {}_7N^{14} = {}_8O^{15} + \gamma\,; \quad {}_8O^{15} = {}_7N^{15} + e^+\\
&{}_1H^1 + {}_7N^{15} = {}_6C^{12} + {}_2He^4
\end{aligned}
$$

The results of the proton collisions are shown on the left. The two equations on the right represent the spontaneous disintegration of the unstable isotopes of nitrogen and oxygen, N^{13} and O^{15}. The succession of reactions may perhaps be envisaged more clearly by setting them out as below.

${}_1H^1 \longrightarrow {}_6C^{12}$	$2{\cdot}5 \times 10^6$ years
${}_7N^{13}$	10 minutes
$\xrightarrow{e^+}$	
${}_1H^1 \longrightarrow {}_6C^{13}$	5×10^4 years
${}_1H^1 \longrightarrow {}_7N^{14}$	4×10^6 years
${}_8O^{15}$	2 minutes
$\xrightarrow{e^+}$	
${}_1H^1 \longrightarrow {}_7N^{15}$	20 years
$\xrightarrow{{}_2He^4}$	
${}_6C^{12}$	

The colliding protons are indicated on the left, the vertical dotted lines represent the nuclear transformations, and the accompanying products, γ radiation ($\dashrightarrow$) or positive electrons (e^+) are shown on the right. The last reaction, whereby C^{12} and He^4 are formed, may be regarded as a fission of the unstable nucleus resulting from the collision of a proton with an N^{15} nucleus. The alternative reaction ${}_1H^1 + {}_7N^{15} = {}_8O^{16}$ is possible, but its relative probability is too small (< 1 in 10^4) to affect the issue.

The times given on the right are the average intervals between reactions involving a given nucleus under the conditions assumed for the centre of the sun. They are approximate estimates, except for those characteristic of the two spontaneous disintegration processes, which have been determined experimentally. It is seen that the complete cycle occupies about 6½ million years. This is small compared with the age of the sun, and we may therefore assume that statistical equilibrium has been established between all the nuclei taking part in the cycle of reactions. Accordingly, their concentrations should be proportional to their mean lifetimes. There is no reliable means of estimating these concentrations in the sun, so that no direct check is possible, but it is at least of interest to compare them with the corresponding values for the earth's crust. If this is a fair sample of the earth as a whole, which is probable, and if the latter is a fair sample of the sun as a whole, which is problematical but not unlikely, we should find some agreement. It turns out that there is good agreement for the $C^{12} : N^{14}$ and for the $C^{12} : C^{13}$ ratios, but not for $N^{14} : N^{15}$. The lifetimes stated lead to a ratio of about $10^5 : 1$, whereas the terrestrial value is of the order of $500 : 1$. This is a serious discrepancy, but the estimated lifetimes are rather uncertain in this case and judgment as to its significance should be reserved until better experimental data become available.

In order to estimate the energy liberated per cycle it is not necessary to consider each reaction separately since the nett result is the formation of a helium nucleus from four protons. The total mass of the latter exceeds that of the former by 0·029 atomic units, or $4{\cdot}8 \times 10^{-26}$ gm. We may calculate the energy resulting from the disappearance of this mass by the Einstein mass-energy equivalence relation, $E = mc^2$, thus obtaining the value $4{\cdot}3 \times 10^{-5}$ erg. It is much more difficult to estimate the total rate of liberation of energy throughout the whole volume of the sun. For this purpose we require to know the temperature and density distribution, and the concentrations of the nuclei taking part in the cycle. The latter are the chief source of uncertainty, since it is not possible to

estimate their abundance reliably even in the outer layers of the sun, owing to the unfavourable location of their chief spectrum lines. All that can be said is that plausible assumptions regarding concentrations lead to values of the right order (*i.e.* ~ 2 ergs per gm. per sec.). Decisive evidence in support of the theory is forthcoming, however, from two other directions.

In the first place, no other conceivable reaction gives a result of the right order. That involving the next lighter element, boron, would give an energy production at least 10,000 times too great, whereas for the next heavier nucleus, oxygen, the rate is some 100,000 times too small. The discrepancy would be still larger for any other reactions, and the carbon cycle is therefore the only possible choice.

Secondly, more positive support is derived from calculations of the temperature coefficient of the carbon cycle, which is found to be of the order of T^{17}, in excellent agreement with that deduced from the observational data for the main stellar sequence. As has been previously mentioned, the temperature coefficient of the proton-proton set of reactions is only about $T^{3.5}$, and as energy considerations rule out any other reactions we may consider the case for the carbon cycle to be conclusively established. It is probable that the proton-proton reactions are predominant for main-sequence stars cooler than the sun, and in the sun itself they may contribute as much as the carbon cycle, but it is certain that for the hotter stars the latter provides the main source of energy. Moreover, it has been shown that the chief characteristics of the main sequence, expressed as relations between mass, radius and luminosity, are also explicable on this basis. It remains to be seen whether the existence of other stellar types can be accounted for in terms of other nuclear reactions, and whether the processes of stellar evolution can be interpreted on the basis of nuclear reactions in general.

The Red Giants and Stellar Evolution

These stars do not conform to the mass-radius-luminosity relationships characteristic of the main sequence. Although there is nothing abnormal about their masses and luminosities, their radii are extremely large and their surface temperatures unusually low, whence of course the tendency to redness. When plotted on a radius-luminosity diagram they cover a considerable range without exhibiting any very obvious regularities, except for certain of them which show periodic fluctuations of luminosity. These fall roughly

along the boundary of the region occupied by the red giants, and occur in three fairly well-defined groups. In each of these the periods are found to be of the same order, either about a day, a fortnight, or a year. They are known respectively as short-period, Cepheid and Mira variables, and all owe their light-variability to a periodic variation of radius, or pulsation as it is commonly termed. Some form of instability is evidently responsible, but the cause of this, and of the well-marked grouping according to periods, have hitherto defied all attempts at explanation.

The fact that the temperatures, central as well as surface, of these stars, are considerably lower than for the sun, suggests that they may draw their energy supplies from nuclear reactions which can be maintained at lower temperatures than that which is necessary for the carbon cycle. There are only six such reactions which need be considered; they arise from the interaction of protons with deuterium (${}_1H^2$), lithium (${}_3Li^6$ and ${}_3Li^7$), beryllium (${}_4Be^9$) and boron (${}_5B^{10}$ and ${}_5B^{11}$). They fall into three distinct classes, according to the temperatures required to maintain them at a sufficient intensity, as follows:

$$
\begin{array}{ll}
(1)\ {}_1H^1 + {}_2H^2 = {}_2He^3 & \text{less than 1 million degrees.} \\
\left.\begin{array}{l}
(2)\ {}_1H^1 + {}_3Li^6 = {}_2He^3 + {}_2He^4 \\
\ {}_1H^1 + {}_3Li^7 = {}_2He^4 + {}_2He^4 \\
\ {}_1H^1 + {}_4Be^9 = {}_3Li^6 + {}_2He^4 \\
\ {}_1H^1 + {}_5B^{11} = {}_2He^4 + {}_2He^4 + {}_2He^4
\end{array}\right\} & \text{2–6 million degrees.} \\
(3)\ {}_1H^1 + {}_5B^{10} = {}_6C^{11} & \text{about 10 million degrees.}
\end{array}
$$

It is a tempting hypothesis, and Gamow has shown that it is a very plausible one, to associate these three temperature groups with the three groups of variable stars. There is little direct evidence, admittedly, but it is possible in this way to account very simply not only for the existence of three groups but also for the gaps separating them and for the phenomenon of variability. The explanation is dependent upon the fact that all the above reactions, unlike the carbon cycle, involve continuous consumption of nuclear "fuel" (other than protons) and therefore its ultimate exhaustion. When this occurs the central temperature will at first fall, but will then be raised again by gravitational energy released by contraction, and this will continue until the temperature has risen sufficiently to start off the next reaction. The transition from one group to the next, during which gravitation supplies the energy, can be shown to be comparatively rapid, which implies that relatively few stars will be found in this condition at any given time, thus accounting satisfactorily for the gaps. The pulsations which give rise to the variability may reasonably be attributed to temperature

instability associated with the passage from the thermo-nuclear to the gravitational type of energy production. So long as one or the other is predominant, as is usually the case, the star is stable, but if they are of the same order of magnitude it is quite likely that a periodic alternation between the two may occur.

Returning now to the sun, we may enquire what the thermonuclear theory can predict as to its future. In the first place, since only protons are being consumed and the hydrogen content of the sun is approximately known, we can estimate its expectation of life at the present rate of consumption. This exceeds 10^{10} years, which is well above its probably present age. But as Gamow has shown, the temperature, and therefore the rate of consumption of protons, is likely to increase by reason of the accumulation of helium formed by the carbon cycle of reactions, since this is less transparent to radiation than the hydrogen which it replaces. He estimates that the solar radiation may be expected to increase one hundredfold by the time the hydrogen is on the point of being exhausted, *i.e.* in about 10^{10} years, after which the luminosity will fall off rapidly as contraction proceeds.

Conclusion

The theory outlined above has clearly opened a new chapter in astrophysics, and is certain to lead to further advances of the most far-reaching character. Apart from its detailed application and development in connection with the study of stars as they are, we may hope with its aid to probe the past and predict the future of the universe with much more confidence than has hitherto been possible. It may well provide also the answer to the question of how the chemical elements themselves came into existence.

Finally, it may be of interest to remark on the connection between this work and that which has recently led to the release of nuclear energy by artificial disintegration of the heaviest elements. The former is concerned mainly with the building up of a light nucleus (He) from still lighter ones (H) by a natural agency, the latter with the breaking down of a heavy nucleus (U, etc.) by an agency-neutron bombardment—which cannot, so far as we know, occur in nature. But both the natural (creative) process and the artificial (destructive) process are fundamentally dependent upon the transformation of nuclear mass into radiation energy, and President Truman was therefore justified in proclaiming (August 6, 1945), that "The force from which the sun draws its power has been loosed against those who brought war to the Far East."

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THE ASSOCIATION OF BASIC "FRONTS" WITH GRANITISATION

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Our present knowledge of the changes that have taken place in the folded belts or orogenic zones of the earth's crust, as a result of granitisation, is firmly rooted in Sederholm's meticulous work on the Pre-Cambrian rocks of Finland. Every student of granitisation will be everlastingly grateful for the magnificently illustrated series of Memoirs in which his observations and deductions are recorded; knowledge advances and interpretations change, yet though twenty years and more have elapsed since their publication, Sederholm's recorded observations of the phenomena of granitisation remain not only unsurpassed but unrivalled.

The oldest rocks of the Svecofennian belt of southern Finland —the leptites—are usually so much altered that their origin is obscure. They are commonly interpreted as bedded tuffs and lavas, varying from rhyolitic to andesitic in composition, but some portions, including intercalated layers of limestone and quartzite, are regarded as being of sedimentary origin. Sederholm traces the gradual transformation, by progressive granitisation, of the leptites to a grey gneissic granite, the "Older Granite," through a series of intermediate stages of mixed rocks, for the designation of which he introduced the term "migmatite." Subsequent to the evolution of the grey gneissic granite a swarm of typical basaltic fissure-dykes was emplaced, some of the members of which cut obliquely across the foliation of their host rock. This dyke swarm is comparable with those of Tertiary age in Britain.

After the emplacement of the basaltic dykes within both leptites and grey gneissic granite, a second period of granitisation ensued, and parts of both the grey gneissic granite and the remaining leptites were transformed *in situ* to the red Hangö granite with its attendant migmatites. Within the Hangö granite the earlier basaltic dykes still remain: sometimes intact, with their original chilled margins preserved; sometimes veined by the newer Hangö granite within which they are now found; and sometimes reduced to a swarm of angular relics in process of dissolution within the Hangö granite.

Individual dykes can be traced from the leptite and grey gneissic granite into the Hangö granite, within which they become increasingly fragmentary (Sederholm, 1926, Plate IX), and finally disappear.

The transformation of leptite into grey gneissic granite, and of the latter, together with its added swarm of basic dykes, into Hangö granite was naturally not accomplished without chemical changes. In each instance the change included addition of alkali, and decrease of other constituents, and, since some of the rocks transformed to Hangö granite were originally of andesitic and basaltic composition, the amount of material transferred must indeed have been large. Sederholm attributed these changes to the agency of granitic ichor, which he envisaged as a granitic juice "showing gradations between an aqueous solution and a very diluted magma," or as "a magma containing much water in a gaseous state." The astounding thing, however, is that each particular granite conforms to a recognisable chemical type, and maintains its composition even where large masses of basic rock have disappeared from within it. The amazing homogeneity of the Hangö granite led Sederholm to deduce that in its formation "assimilation" of a diversified assemblage of country rocks by ichor must have been followed by some form of differentiation. Although he left unsolved the problem as to the method whereby this differentiation, involving the displacement and removal of cafemic* materials, might have been achieved, he nevertheless threw out a significant suggestion as to where the solution might be sought when he wrote: "The basic rocks dissolved in the granite seem to disappear as by magic, perhaps escaping together with the volatile or fluid constituents. Only in rare cases phenomena are observed that seem to give an indication of what has happened. So the 'basic halos' around fragments in the Obnäss granite tell of a diffusion extending to a certain limit. In greater fragments in the same granite the femic constituents have been concentrated in certain parts, which have even received an ultrabasic composition."

Continued field work, both in Fennoscandia and in Greenland, finally yielded the clue as to the destiny of the cafemic constituents displaced during migmatisation. Both leptites and sedimentary rocks in the peripheral zones of migmatite regions were found to be enriched in mafic† minerals such as cordierite, garnet and biotite. Wegmann (1935) correlated this Fe-Mg enrichment with the loss of Fe and Mg from the rocks overcome by migmatisation, and for this zone of enrichment in cafemic constituents he coined the term "Mg front." Thus the view originated that the development and

* Cafemic: a term for an assemblage of Ca, Fe and Mg.

† Mafic: a term applied to minerals rich in Mg and Fe.

upward progress of migmatites in orogenic belts is accompanied by a frontal zone of Fe-Mg enrichment. Such a correlation naturally cast doubt on the concept of "granitic ichor" as the postulated active agent in such transformations, and it became fashionable, in the absence of exact knowledge of the processes involved, to write the word "ichor" between inverted commas, or to substitute for it "molecular migration," or the noncommittal term "emanation." Wegmann believed the transformations concerned, which are far too intimately interwoven in the bodies of the rocks to be explained as a result of injection, to have been accomplished as a result of migrations of material through an intergranular film. As small-scale examples of complementary granitic and basic zones, resulting from such migrations, he drew attention to the biotite-rich selvedges that rim the granitic veins and pod-shaped bodies in migmatite regions.

It is not only the leptites, and pelitic* and semi-pelitic sediments, however, that experience enrichments in Fe and Mg as the frontal zone of migmatisation advances. At approximately the same time as Wegmann observed the basification of these rocks in the forefront of migmatisation, Backlund was studying the successive changes suffered by limestones (1936 *a*), and by basaltic rocks and their tuffs (1936 *b*), under similar circumstances. He found that the migmatisation of limestones commences with the fixation of constituents including Fe, Mg and Si, with concomitant displacement of Ca and CO_2. In consequence the limestones gradually become converted to amphibolites, and only subsequently do the latter become granitised. Similarly he traced the basaltic rocks and their tuffs through the following progressive series of transformations: basalt $\rightarrow$ uralite-porphyrite $\rightarrow$ greenstone $\rightarrow$ amphibolite $\rightarrow$ garnet-amphibolite, and correlated the respective chemical and mineralogical changes with successive stages of the advance of the migmatite "front." The further development of eclogite-amphibolite from garnet-amphibolite he found to depend on the additional factor of extreme dynamic pressure; eclogite itself developing as the final stage of alteration under extreme conditions of both dynamic pressure and high temperature. Subsequently amphibolite, eclogite-amphibolite and eclogite, as the case may be, may become granitised, the displaced cafemic constituents being once again driven out to the new frontal zone of migmatisation. These observations of Backlund and Wegmann apply not only to the Pre-Cambrian orogenic belts of Fennoscandia, but also to the granitisation

* Pelitic rocks are those initially of sedimentary origin rich in alumina.

associated with the Caledonian orogeny in Greenland and in Scandinavia.

Recently (1943, 1946*a*) Backlund has made a collected and correlated story of the sequence and interdependence of the progressive changes undergone by the Pre-Cambrian rocks of Fennoscandia through the successive orogenic cycles. He shows that the leptites can only be satisfactorily interpreted as alteration products of psammitic* and pelitic sedimentary rocks. This conclusion is based on (*a*) their field associations—they contain intercalated layers of limestone and quartzite; (*b*) their chemical composition—they are not only abnormally rich in SiO_2 as compared with acid volcanic rocks, but also abnormally rich in Al_2O_3; (*c*) their mineral composition and microscope textures; and (*d*) their development in at least three of the four Pre-Cambrian orogenic belts of Fennoscandia. As seen in their leptitic guise, however, the original sediments are now so much altered as to have a superficial resemblance to altered acid volcanic rocks. From this initial stage of alteration—leptitisation—Backlund traces the Pre-Cambrian sediments through successive cycles of more intense granitisation, during which first, the "Older Granite" and subsequently the younger granites were evolved. He shows from the chemical compositions of the rocks concerned that each granitisation involved displacement of Fe, Mg and Ca from the granitised material, and concentration of K within it. With this progressive removal of cafemic constituents Backlund correlates the transformations of limestones and basaltic rocks alike to amphibolites, and the successive stages of enrichment of pre-existing sedimentary iron-ore deposits and skarns.† The processes of diffusion, dependent on successive replacements with complementary displacements and migrations, he regards as ionic migrations facilitated by the presence and development of imperfections of the crystal meshes (*cf.* K. Lonsdale, SCIENCE PROGRESS, 1947, **35**, 1).

Such correlated changes of granitisation and basification are, however, by no means confined to the Pre-Cambrian of Fennoscandia. Not only do the rock associations in other Pre-Cambrian terrains reveal that similar processes have been at work, but the similarity between the rock associations in orogenic belts of all ages indicates that such processes are characteristic of every orogeny. Reference may be made to the association of granite and granite-gneiss with

* Psammitic rocks are those initially of sedimentary origin rich in silica.

† Skarn: an old Swedish term meaning wreckage. It is applied to mineral aggregates, rich in Fe and Mg, developed by reconstruction of pre-existing rock.

schists enriched in Fe, Mg, Ca and Na in the Archaean of India. Dunn (1942) correlated this enrichment with losses from zones of granitisation, and introduced the term "diabrochite" to describe the basified and felspathised schists which form the complements of migmatites. Again, in the Haliburton-Bancroft area of Canada, granites and gneissic granites are associated with amphibolites, the latter having been shown by Adams (1909) to be derived both from limestone and basaltic rocks; chemical analyses indicate that the conversion of limestone to amphibolite involved introductions including Fe and Mg.

Turning to our own country, it is clear that recognition of these complementary processes of granitisation and basification will have a useful application in the deciphering of the rock associations within each of the British orogenic belts. A glance at the beautiful photographs (Plates VI–XIV) illustrating the North-West Highland Memoir reveals striking similarities between the Lewisian rocks of the North-West Highlands and those of the Pre-Cambrian of Fennoscandia. Within the Lewisian there is a highly suggestive association of contrasted rock types; rocks such as amphibolite, garnet-amphibolite, hornblendite and pyroxenite occurring as bands and fragmentary inclusions within leucocratic gneiss, against which they may either exhibit sharp boundaries or show gradational contacts suggestive of their dissolution within the gneiss. Similar relationships between the basic and acid components of the Pre-Cambrian gneiss of the Mona Complex, Anglesey, have been described by Greenly; and, moreover, within the basic relics, narrow ultrabasic selvedges around pegmatite veins and pods (Greenly, 1923, Figs. 4, 5 and 6) provide small-scale evidences of diffusion of Fe and Mg.

Turning to the rocks of younger orogenic belts in Britain: the complementary processes of granitisation and basification may explain the association of granulites, migmatites, amphibolites and basic hybrids in Sutherland. Much research has already been accomplished on the Highland migmatites (Horne and Greenly 1896; Read, 1931; Cheng, 1944), but only now is an attempt being made to separate the epochs of migration, and to trace the destiny of the cafemic constituents displaced during migmatisation (work in progress by H. Y. Ma). The idea that migmatites are to be explained by the injection of granitic or trondhjemitic "juice" has been held so strongly in Britain that the prescient suggestion, made as far back as 1903 by Greenly, relating the phenomena of granitisation in Sutherland to a process of solid diffusion, passed unnoticed, and a logical interpretation of the basic components of

the complexes was thus postponed for nearly half a century. Yet small-scale phenomena indicative of solid diffusion—the margining of granitic veins by biotite-rich selvedges—have more than once been recorded (Read, 1931).

The application of these modern conceptions of granitisation to the interpretation of the rock associations of the Grampian Highlands also remains to be tested by detailed chemical work. The aureoles, characterised by staurolite, kyanite, almandine and biotite, which surround the migmatites (" Older Granites ") of Aberdeenshire and Perthshire, may well be diabrochites developed in advance of the zone of migmatite formation. Indeed, some evidence that such is the case can be found in the observations (*a*) that the Loch Tay Limestone, and its eastern equivalent the Deeside Limestone, show distinct chemical change, as judged by their mineralogy, when traced from west to east, and (*b*) that the epidiorites show a marked increase in Fe relative to Mg (Wiseman, 1934) as they are traced from the biotite to the garnet zone. Further, it has already been demonstrated that the albite-schists of Antrim and the South-Western Highlands, and the biotite-rich schists with which they are associated, are chemically unlike any known sedimentary or igneous rocks. These rocks are located at the nose of the recumbent Carrick Castle fold, and the biotite-rich schists represent the advance of a K-Fe-Mg-Al front which moved ahead of a Na-Si front, now represented by the albite-schists, in the direction of the axial plane of the fold (D. L. Reynolds, 1942). Both of the rock types represent an advance-guard of ionic migrations moving ahead of a zone of migmatites which, together with the axial plane of the main body of the fold, has since been removed by denudation from the South-Western Highlands, though the migmatite zone is still exposed in the " Older Granite " of Perthshire and Aberdeenshire.

Reference should also be made to the Hercynian orogenic belt of south-western England. Many of the Cornish greenstones—amphibolites—are chemically unlike either unaltered basic igneous or sedimentary rocks. Their abnormally high content of iron oxides, amounting, in some examples, to as much as 25 per cent., probably bears witness to the advance of the Fe front into this marginal zone of Hercynian folding (D. L. Reynolds, 1947).

In many recent papers and reviews there has been a tendency to confuse granitisation with the effects of supposed injections of granite magma, disguised under the name juice or ichor. It is, therefore, necessary to stress the fact that granitisation depends, not on the bodily introduction of magma, juice or ichor, but on a complex series of ionic migrations, with balanced additions and

subtractions, so that as the rocks undergoing granitisation approach the composition of granite, others receive additions including Fe and Mg, and become more basic. The recognition of these processes opens up wide fields for petrological research on rocks of all types, and of all ages, in the British Isles. Even the cementation of sandstones, and many other still obscure effects of diagenesis,* may be high-level expressions of the final stages of the activity initiated far below by ionic migrations.

Something further should perhaps be added in explanation of the use of the term *front*. Just as the conception of a military front changed between the two world wars, so the geochemical meaning of front has been expanded as knowledge of the details of the advance of granitisation has widened. A front occurs wherever there is a diffusion limit marked by a change in the mineral assemblage. Thus inclusions of country rocks within the granite represent isolated strongholds inside country otherwise already occupied. On the other hand, granitic pods developed within the country rocks beyond the main line of advance of granitisation correspond to territory held by paratroops. Around the isolated strongholds of resistance, beyond the main zone of frontal attack, and between the paratroops and the opposing forces, fronts occur. Similarly, relics within the granite, the zone of country rock margining the main region of granitisation, and the country rocks encasing the granite pods, become subjected to the advance of an Fe-Mg front, and may finally either be by-passed by the "invading" granite, or become more or less granitised. Fe-Mg fronts are particularly strongly developed within the rocks that were initially relatively basic, and, in consequence, these rocks commonly remain as highly basic or ultrabasic relics within granite.

The interdependence of processes of granitisation and basification, the recognition of which was based primarily on field observations, has recently received strong geochemical support from a statistical study by Lapadu-Hargues (1945) of the chemical compositions of rocks of varying regional metamorphic grade. Irrespective of the age of the rocks concerned, he has collected together the chemical analyses of the following groups of rocks: shales and phyllites; low-grade schists characterised by chlorite and sericite; biotite-muscovite-schists; gneiss with two micas and felspathised varieties of mica-schist; granite-gneiss; granite and muscovite-biotite-granite. Lapadu-Hargues finds that the distribution of chemical elements throughout these groups of rocks can be correlated with

* Diagenesis: a term denoting the changes that bring about the consolidation and cementation of sedimentary rocks.

the metamorphic grade. Thus Fe and Mg are concentrated in the frontal zone of regional metamorphism, within the first four groups of rocks named above. Total alkalis, relative to alumina, increase progressively from the low to the high grade rocks; Na increases relative to K in the four lower grade groups of rocks, K being concentrated in the granitoid gneisses, granites and muscovite-biotite-granites. Ca increases steadily as the metamorphic grade increases, reaching its maximum concentration in the granites. Lapadu-Hargues correlates this distribution of the elements, which is evidently dependent on their relative mobilities, with their respective ionic radii, the smaller ions having migrated the farthest. He finds the order of increasing mobility to be: K, Ca, Na, Mg, Fe.

So far the discussion has been restricted to the syntectonic phase of "igneous" activity. The association of basic fronts with granitisation is, however, equally characteristic of the post-tectonic granite bodies; granite stocks being commonly rimmed by an aureole of enrichment in femic or cafemic minerals. Where the granite is emplaced in pelitic sediments, the aureole is commonly enriched in biotite, or in biotite and cordierite, which, in extreme cases, may form more than 50 per cent. of the rock. Where the country rock includes basic igneous types the aureole is even more markedly enriched in basic components, and is then characterised by pyroxenes or amphiboles. Thus, in contact with the granites of north-eastern Minnesota, the Ely Greenstone is converted to highly basic amphibolite containing up to 95 per cent. of amphibole; the andesites within which the Copper Mountain stock, British Columbia, is emplaced are markedly enriched in both augite and biotite; and the Moine granulites (associated with hornblendic rocks) surrounding the Cnoc nan Cuilean syenite, Sutherland, are enriched in both ægirine-augite and hornblende. Where limestone forms the country rock to post-tectonic granitic intrusions it is commonly converted to amphibolite or to skarn with which ore deposits may be associated. An extreme example of enrichment of rocks of diversified origin in Fe and Mg is found in the aureole surrounding the Orijärvi granite, Finland, where leptites have been converted to cordierite-anthophyllite rocks, amphibolites to cummingtonite-amphibolites, and limestones to tremolite skarn.

In order to explain the aureole of Fe-Mg enrichment around granite stocks, it has to be assumed either (*a*) that considerable proportions of Fe and Mg remain in the residual solutions of granite magma, which is contrary to experimental evidence; or (*b*) that gaseous or volatile compounds of Fe and Mg are given off from granite magma, *i.e.* that the process is one of pneumatolysis; or

(c) that the aureole of Fe and Mg enrichment is a basic front, to be explained by the fixation of material that migrated from a central locus, now occupied by granite, at the time the granite was emplaced; the granite itself representing, not a crystallisation product of magma, but the granitisation product of the country rocks within which it occurs. Small-scale evidences that (c) is the correct interpretation have already been found. A sedimentary raft, within the granite of the Newry complex, contains pod-like bodies of granite, each rimmed by a narrow zone in which the enclosing sediment is conspicuously enriched in mafic minerals. The granite pods, which measure up to 2 or 3 feet across, show sharply cross-cutting relationships to the sedimentary bedding, so that it is clear that portions of the sediments, now represented by granite, have disappeared. Since it is impossible that such enclosed bodies of sediment can have been mechanically removed, it is evident that the sediment has been transformed to granite. By comparison of chemical analyses of the sedimentary bands, and of the granite of the pods along the same line of strike, it has been demonstrated that all that was required to convert the sediments to the particular granites of the pods was a small addition of Na, Ca and Si, balanced by loss of Al, Mg, Fe, K, H, Ti, P and Mn. Furthermore, the chemical analysis of the rock of one of the rims demonstrates that, in its formation, the material added to the sedimentary rock is qualitatively similar to that lost from the granitised pods (D. L. Reynolds, 1943). The only tenable interpretation of these granite pods and their complementary basic rims is that they originated by a process of solid diffusion involving ionic migration. Granite stocks and their basified aureoles are then naturally to be regarded as large-scale expressions of the operation of similar processes.

Further, many of the granite stocks belonging to the post-tectonic phase of activity are capped by basic and ultrabasic rocks. These rocks characteristically exhibit metamorphic textures, together with a clouding of their more lime-rich plagioclases with iron-ore dust. These textures have, in the past, been interpreted as evidencing the thermal alteration of the rocks concerned; the " magma " of the granite emplaced beneath being regarded as the source of heat. That this cannot be the explanation of the crystalloblastic textures is evidenced by the fact that whereas such textures are strongly developed towards the sediments, they disappear, the textures becoming more normally " igneous " in aspect, as the granite is approached. Moreover, the basic roof rocks commonly show every gradation to the acid types. Further, the supposition that the rocks of these stocks were emplaced as magmas disregards the space

problem. If it is conceivable that granite magma may have stoped its way into its present position, the displaced blocks of earlier emplaced rocks sinking down through the liquid, it is certainly not conceivable that magmas of the more basic varieties could have stoped their way into position. Such magmas would have a higher specific gravity than most of the country rocks that would have to sink through them. Yet many of these highly basic rocks are characterised by inclusions of sediments having a lower specific gravity than the enclosing rocks ; such inclusions can be interpreted only as relics of the material that was basified.

Detailed field, microscopic and chemical study of the Caledonian post-tectonic batholith of the Newry area (D. L. Reynolds, 1934, 1936, 1944, 1946) have furnished evidence that the layered basic and ultrabasic roof-rocks represent an Fe-Mg-Ca front proceeding in advance of one of granitisation. A progressive molecular desilication (relative to the molecular proportion of the bases present) of an assemblage of pelitic and semi-pelitic sediments is seen in the gradational passage : sediment $\rightarrow$ mobilised sediment $\rightarrow$ syenite $\rightarrow$ monzonite $\rightarrow$ shonkinitic monzonite $\rightarrow$ biotite-pyroxenite. The desilication change from sediment to syenite is predominantly one of enrichment in alkalis, whilst the further desilication change from syenite through monzonitic types to biotite-pyroxenite is essentially one of enrichment in Fe, Mg and Ca. All these rocks exhibit crystalloblastic textures indicative of a metamorphic origin. From the biotite-pyroxenite there is still further gradation through garronite to hypersthene-monzonite, the two latter rocks being chemically intermediate between biotite-pyroxenite and the adjacent granite (granodiorite). The latter gradational series exhibits more normal igneous textures than the former, and represents a granitisation change. Thus, in the Newry area, as a post-tectonic granite body was emplaced it was preceded by a zone of molecular desilication of the country rock sediments (the basic front) composed of an outer aureole of enrichment in alkalis, and an inner one of enrichment in Fe, Mg and Ca. Fe, Mg and Ca, fugitive from, and fixed ahead of, the centre of granitisation, themselves displaced alkalis, the fixation of which in a frontal zone gave rise to the syenite.

For the development of such basic roof-caps great quantities of Fe and Mg must be mobilised, and in this connection a recent discussion of Backlund's (1946b) is pertinent. Backlund draws attention to the fact that the mean composition of a sedimentary pile of shales, sandstones and limestones is deficient in Fe, Mg and Na as compared with the mean composition of the "igneous" rock suites evolved therefrom. This is particularly the case when the basic

components (basic fronts) are of considerable volume, and when the acid component is granodiorite rather than granite. Backlund regards geosynclinal basaltic rocks (including ophiolites), emplaced within the sedimentary pile, as supplementary sources of Fe and Mg. He outlines the role of the basaltic rocks as follows. After an initial amphibolitisation of the basaltic rocks, as described above, a subsequent granitisation will give rise to a new basic front of greater magnitude and diversity. Given appropriate temperature conditions, with not too steep a gradient, the displacement and migration of basic constituents from the already basified basaltic rocks, and their differential fixation within the diversified sedimentary layers, contributes to the formation of groups of rocks, of intermediate composition, characterised by one or more of the following rock types: monzonite, quartz-diorite, mangerite, anorthosite, etc. The composition of some of these rocks is such that they may ultimately become rheomorphic,* and be transposed to higher levels either as minor intrusions or as effusive rocks. According to Backlund, iron ore deposits of sedimentary origin appear to be extremely resistant to granitisation. During early granitisations they tend to become increasingly enriched in iron ores and other components characteristic of basic fronts. When eventually they do succumb to granitisation the basic materials of which they were composed contribute to the development of late iron silicates, such as the skarn minerals andradite, grunerite, knebelite, etc., in the newly forming basic front. Backlund compares the process of granitisation to a chain-reaction: an initial small addition of Na and Si to the least-resistant sediments, the pelitic rocks, is sufficient, under appropriate temperature and pressure conditions, to give impetus to the whole string of reactions.

A recent study (D. L. Reynolds, 1946) of chemical data relating to the alteration of pelitic and psammitic sediments, and of basic igneous rocks, occurring in the aureoles surrounding granite masses, and also as inclusions within the granite masses themselves, has revealed the fact that in every example for which adequate chemical data exist, the emplacement of granitic bodies has been accompanied by the introduction of cafemic constituents and alkalis into both aureoles and inclusions. Only subsequently have these initially basified rocks been granitised. Examples of zoned inclusions with granitised rims, and cores that are basified as compared with the unaltered rocks from which they were derived (including one with

* A rheomorphic rock is one that has become partially or completely mobilised or fused as a result of the introduction of migrating materials with concomitant rise of temperature.

an intermediate zone, between the basic core and the granitised rim, that is even more basic than the core), indicate that the process of alteration was one of diffusion, whereby material displaced from the rim of each inclusion during granitisation was driven inward and fixed internally. Moreover, since the inclusions retain their sharp margins during the initial stages of basification and granitisation, it is clear that the processes of replacement depended on diffusion through the solid, the intimacy of the replacement suggesting ionic diffusion. The presence of sharp contacts is so commonly cited as if it constituted evidence against granitisation that it should be emphasised that such sharp margins not only present no difficulty or inconsistency, but are actually to be expected as boundaries to replacements dependent on solid diffusion.

From the analysis of relevant chemical data it is apparent that a basic front is, in fact, a zone within which the chemical bases have increased to such an extent that the rock has become molecularly desilicated relative to the molecular proportions of the bases present. When a basic front is developed within pelitic sediments there is sometimes an initial stage, in time or in space, of enrichment in alkalis, followed by enrichments including Fe, Mg and Ca. In the first stage of change the rocks are felspathised, and may attain the composition of syenite, whereas in the second stage of change the rocks are basified, and may ultimately attain the chemical composition of basic or even ultrabasic rocks. Within the basic front the chemically transformed rocks may acquire a higher percentage of one or more constituents than that characterising either the parent rock (whether it was originally of sedimentary or igneous origin), or the adjoining granite. For such an increase the term "geochemical culmination" has been proposed. Geochemical culminations of one or more of the minor constituents Ti, P and Mn characterise the basified rocks of the zone of desilication, and will henceforth serve as useful criteria for the recognition of basified rocks evolved as a result of ionic migrations in the forefront of granitisation.

One of the major petrogenetic problems of kratogenic igneous activity, that is of igneous activity in the relatively stable regions located beyond the limits of the orogenic belts, is the association of basic rocks (basalts, dolerites and gabbros) and younger acid rocks (rhyolites, granophyres and granites), with intermediate types but feebly developed, and these demonstrably of hybrid origin. In important discussions of the Arctic Tertiary basalt plateau, Backlund (1942, 1944) has indicated the applicability of modern conceptions of granitisation to the interpretation of these rock associations. In

east Greenland (Backlund, 1937) basalts of Upper Cretaceous and Tertiary age are invaded by granite which Backlund believes to be a product of granitisation of post-Devonian sediments. Where in contact with the granite, the basalts become gabbroic, being coarsely ophitic, with augite crystals several centimetres in diameter. Inclusions of the basic rocks within the granite, moreover, are converted first to coarse-grained peridotite, and subsequently to coarse-grained hornblendite. These changes involved not only basification of the initial basalt, but also its desilication, for the silica content diminishes from 48–52 per cent. in the initial basalt to 38–42 per cent. in the ultrabasic rocks.

Backlund (1942, 1944) adduces evidence indicating that the Arctic basalt plateau is built up, not merely of a sequence of lava-flows as previously supposed, but largely, and particularly in the early stages, by a gigantic pile of sills of basaltic composition, emplaced within sedimentary rocks of Mesozoic age. He points out that the emplacement of the sills must have been accompanied by an important transference of heat into the upper sedimentary layers, and that this great heat transference would have the following important consequences: (1) The basaltic sills last emplaced would crystallise under heat conditions comparable to those obtaining in depth, and, in consequence, would solidify as coarsely crystalline rocks. (2) As the temperature rose, the volatile constituents of the sedimentary layers would become mobilised, and induce a recrystallisation in the basaltic layers. (3) At still higher temperatures the mobilisation of alkalis would lead to granitisation of the sedimentary layers, sometimes accompanied by rheomorphism and the development of hybrids. (4) Fe and Mg displaced by the granitisation of the sedimentary layers would be fixed in the basic sills, which might, in consequence, even acquire an ultrabasic composition. In this connection Backlund emphasises the trivial contact alteration associated with the ultrabasic rocks, an observation at variance with the high temperatures that must have been attained if the ultrabasic types had been emplaced as magmas.

With a shrewd grasp of significant correlations, Backlund has hinted at the applicability of such interpretations to the rock associations of the British Tertiary province. In this connection it is, therefore, of interest to record that work now in progress on Slieve Gullion, Northern Ireland (D. L. Reynolds), is demonstrating his outstanding clarity of perception. Slieve Gullion is built of an alternation of practically horizontal layers of dolerite and granophyre, some of which are multiple. Many of the dolerite layers are demonstrably sills, with chilled margins against the granophyre.

Yet the dolerite layers are not only veined by the granophyres, but, in their crystalloblastic textures they exhibit strong evidence of recrystallisation, of the type usually attributed to contact alteration. Clearly the dolerite layers cannot have been both chilled against and "baked" by the adjacent granophyre. It has, however, already been shown (D. L. Reynolds, 1937) that the granophyre at one horizon on Slieve Gullion has been developed *in situ* from Caledonian granodiorite, and that the transformation has culminated in rheomorphism, as is evidenced by the veining of the dolerite by the granophyre. Thus, in their present form, both the dolerite and the granophyre are metamorphic rocks. The only logical interpretation, therefore, is that the dolerite layers were originally emplaced and chilled against the antecedents of the present-day granophyre layers, and that the whole rock suite was subsequently granitised. Granitisation would account for the development and rheomorphism of the granophyre, whilst the complementary process of basification would account for the crystalloblastic textures of the dolerite, and its enrichment in biotite and amphibole. Such changes become less surprising when it is realised that the rocks under discussion occupy the site of a Tertiary volcanic caldera.

Following up Harker's work in Skye (*Skye Memoir*; see especially Figs. 38 and 39, pp. 189 and 190), McIntyre (1947) has observed similar relationships between sheets of marscoite and granophyre. Marscoite layers, with chilled edges, occur within a younger granophyre by which they are invaded, and within which they appear as sheet-like relics, traceable along their strike into agmatites, formed *in situ*, composed of fragmentary relics of marscoite within the replacing granophyre. Although in a different milieu, these rock associations are comparable with the association of leptite (or grey gneissic granite), basaltic dykes and Hangö granite described by Sederholm, and referred to at the beginning of this article.

In a recent discussion of granitisation, Niggli (1946) has emphasised the loss of Fe, Mg and Ca that is implied, saying "it is above all difficult to solve the question whither the Fe, Mg and Ca have wandered." In this connection one cannot do better than quote Sederholm. "Purely theoretical deductions, whether they may be based on geophysical or chemical considerations, cannot lead to any definite solution of these problems, nor can laboratory experiences do so. The safest way in geology is the old way of inductive science, by studying nature's methods in her own great workshops, where they are available to our observation . . . conjoined with microscopical research, and, of course, giving due consideration to the important results of modern physico-chemical science." By follow-

ing these very methods, exponents of granitisation have already solved the riddle of the displaced Fe, Mg and Ca.

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THE BRITISH RAIIDÆ

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Skates and rays (Raiidæ) are valuable and important food fishes which, until quite recently, were despised and neglected. Montagu, writing in 1809, comments upon the large numbers of rays and skates caught around the shores of Devon and Cornwall and says that they were then used chiefly for baiting crab pots. In times of scarcity some of the small ones might be eaten by fishermen's families but were never exposed for sale.

Fifty years later this state of affairs had changed but little. Jonathan Couch, writing in 1862 [1, Vol. I, p. 84], reports that rays and skates were included amongst the "Rabble Fish" that were rejected from the fishmarkets and adds: "The Skate is the largest, and, on the whole, the most important of these rejected fishes, and the Saxon word *Skitan*, to reject, is expressive of the fact of its being so. The same word is the parent of several expressions still in common use as significant of being thrown out, aside, or rejected." Again (*loc. cit.*, p. 89), in writing specifically of the Blue Skate, *Raia batis*, he says: "The Skate is never the special object of the fisherman's search and when it chances to take the hook it may give him perhaps a greater amount of trouble than the prize can repay."

During the succeeding quarter of a century the fish-eating public in this country must gradually have grown aware of the value of rays and skates as food fishes, for Day [2, Vol. II, p. 335], writing some time between 1880 and 1884, refers to Couch's account of rabble-fish and adds the significant statement, "Things are altered now, much of this rabble-fish going to Billingsgate and other large inland markets."

Nevertheless, rays and skates even then were not considered to rank as proper food fishes. Cunningham, in his *Natural History of the Marketable Marine Fishes of the British Islands*, published in 1896, dismisses them with only a few words in the opening general section of the book. In the main part of the work dealing with the history of particular fishes they find no place. McIntosh and Masterman also, in their *Life Histories of the British Marine Food Fishes*, published in 1897, all but ignore the Raiidæ, though they

discourse at length on such unimportant Teleosteans as the gobies, rocklings, sticklebacks, and blennies.

By the beginning of the present century, however, a strong demand for rays and skates had arisen, especially from fish restaurants, and these fishes (collectively) soon ranked amongst the first half-dozen or so of the country's economic species—a place they still hold. In the extreme south-west of England, in the counties

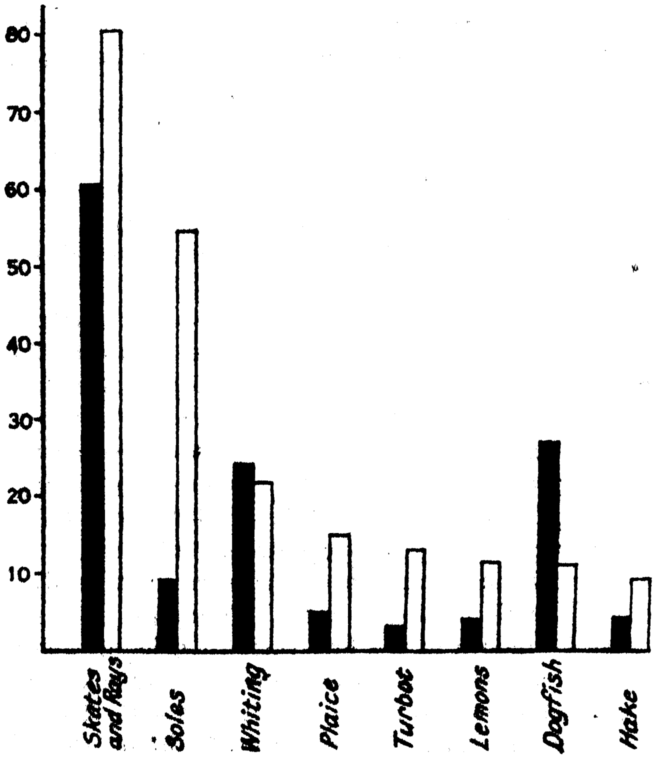


FIG. 1.—Graphical representation of the landings of the principal species of demersal fish of British taking landed in Devon and Cornwall in 1929—a typical year—showing (a) the quantity (black columns) in thousands of cwt., and (b) the value (white columns) in thousands of pounds sterling. Note the leading position of skates and rays.

of Devon and Cornwall, rays and skates are of primary importance, contributing approximately one-third of the total (in both quantity and value) of all demersal fish landed at all ports (Fig. 1). At the port of Newlyn in Cornwall, where nearly 40,000 cwt. of demersal fish is landed annually, over 60 per cent. of this total in a normal year consists of skates and rays.

Skates and rays (Raiidæ) are demersal Elasmobranch fishes in which the body is much flattened dorsi-ventrally (depressed). The

head, trunk, and greatly enlarged pectoral fins are all joined together to form a "disc," whose outline varies from more or less quadrangular to nearly circular, and from which a feeble tail, with two tiny dorsal finlets, projects as a comparatively slender appendage. The gill openings as well as the mouth are on the ventral surface of the body.

In these fishes the pectoral fins have become the effective swimming organs. But for slow movement on the surface of the sea floor the small pelvics are used like feet to push the fish slowly along. With a vigorous thrust they also help the fish to get under way when leaving the bottom quickly from the resting state.

Occurrence and Distribution on the Fishing Grounds

Just over a dozen species of the genus *Raia* occur in British waters. Of these no less than eleven species are found around the shores of Devon and Cornwall, and it was chiefly in the Devon-Cornwall area that the work on which this paper is based was carried out.

At all seasons of the year rays and skates are caught on the usual fishing grounds with little variation in numbers, apart from that caused by the effect of weather conditions on fishing effort. This indicates a minimum of migratory movement, at any rate on a large scale. As a general rule, also, although one species may predominate, several species are present on every fishing ground and appear all mixed up in the catches. But in certain restricted areas only one species may at times be present and even only one sex. On one occasion a long-liner landed a catch at Newlyn consisting entirely of female *Raia fullonica*. In a unique fixed net fishery for rays near Plymouth in the first three months of each year, the catches consist almost entirely of female thornbacks (*R. clavata*) for most of the season and almost entirely of male fish at the end of it (see table on p. 227). There can be no doubt, therefore, that rays often form separate groups consisting of only one species and even, at times, of only a single sex. Such segregation of species and sexes is not noticeable, however, in ordinary circumstances, because several or even many different groups will contribute to a single catch which, when it arrives on deck all thoroughly mixed up, gives no indication of the order in space and time in which the different fish were captured. An unmixed catch can be expected by trawling and long-line fishing (the chief methods) only in the following circumstances: (1) the formation of a single, large, unmixed group spread over a very wide area; (2) the occurrence of a small group alone in a large area untenanted by other rays; (3) the presence of a single, unmixed, group, small or large, on an

isolated fishing ground. These conditions are seldom encountered. Nevertheless, hauls consisting almost entirely of one sex of a single species are occasionally made by both trawlers and liners.

On most of the larger fishing grounds, although one species may predominate, several species are generally present. An attempt has been made to discover whether in such mixed populations the various species mingle indiscriminately, or whether they keep

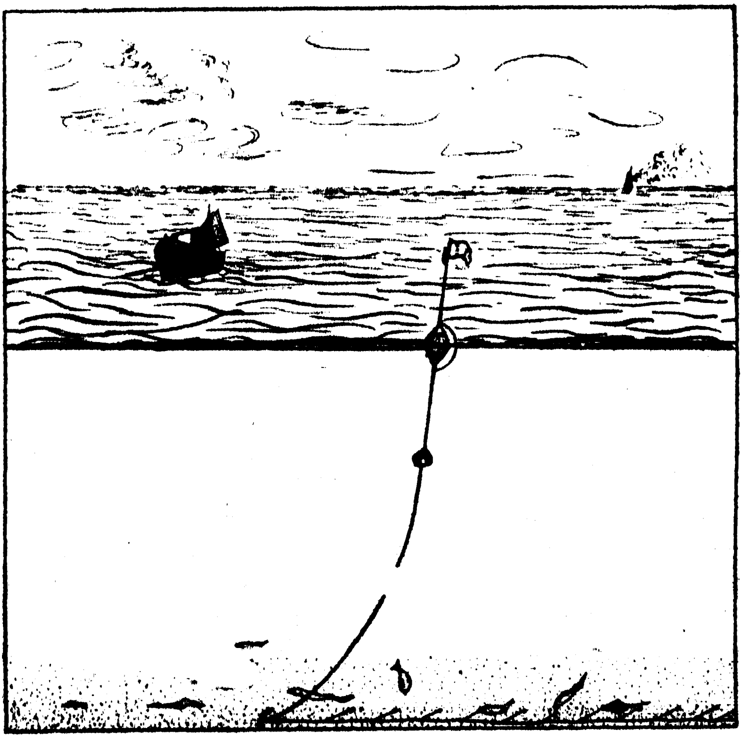


FIG. 2.—Diagram of a Cornish motor liner and a small portion of its long-line that has just been "shot." The vessel remains within sight-range of the dahn flag while the line is allowed to fish. This line carried about 2,600 hooks and stretched for nearly six miles over the sea floor. For further explanation see text.

together in uni-specific groups or shoals. This was done by studying catches of Cornish long-liners, noting the identity of every fish as it came on board, and recording every empty hook. These long lines, or "great-lines" as they are sometimes called, are almost 6 miles long and carry over 2,000 hooks on short snoods at intervals of about 2 fathoms. When the line is shot the hooks, properly baited, lie in a long straight row on the sea floor, where they are left for several hours and then hauled up again (Fig. 2).

If the various species are in separate shoals or groups there should be a tendency for the same species to appear more or less together on the same part of the line. Any such grouping will always tend to be obscured, of course, by the fact that the lines remain on the sea floor for anything up to six hours at a stretch. Therefore, even though at the outset there may be a definite distribution of the species along the line, other fish, or shoals of fish, will come along and take the hooks which have not previously been occupied. Thus the distribution of fish caught on the lines at any particular point of time—unless they occupy adjacent hooks, which is unlikely—will be obscured by those that were hooked either previously or subsequently. There is also the possibility that, purely as a result of chance, two or more fish of the same species may occur together here and there on the line, though the population be entirely and indiscriminately mixed.

An examination of the distribution of fish along numerous fishing lines reveals a definite tendency for the same species to appear more or less together on the lines. This grouping is too pronounced to be explained purely as a result of chance.

In Fig. 3A is shown diagrammatically the catch of fish on a continuous section of line $1\frac{1}{2}$ miles in length, hauled during the forenoon of July 22, 1931, on a fishing ground roughly 80 miles S.S.W. of Mousehole, near Newlyn, Cornwall. Each short vertical stroke denotes a hook which came up empty. A stroke produced downwards indicates a hook on which a fish of some kind other than *R. montagui* was taken, while a stroke produced both downwards and upwards and ending above in a large dot denotes one on which *R. montagui* was taken. It will at once be seen that this fish shows a very definite grouping on this part of the line. A similar grouping of *R. montagui* is shown in Fig. 3B on a half-mile stretch of line hauled during the afternoon of July 23, 1931, on a different ground. Diagrams constructed in like manner for other species provide similar results.

It appears, therefore, that, on the sea floor, where various species of Raia are present within a limited area at the same time, the species do not mix indiscriminately, but segregate into uni-specific groups or shoals.

MIGRATIONS

As yet little is known regarding the migrations and shoaling habits of the Raiidae. What little information there is on record applies mainly to *Raia clavata*, perhaps because its movements are more marked than those of the other species, or perhaps because it

is the most generally distributed and most abundant ray in inshore shallow waters and at moderate depths down to at least 80 fm. Meek [4, p. 41] states definitely that there is, in this species, a periodical migration inshore in summer and into deeper water

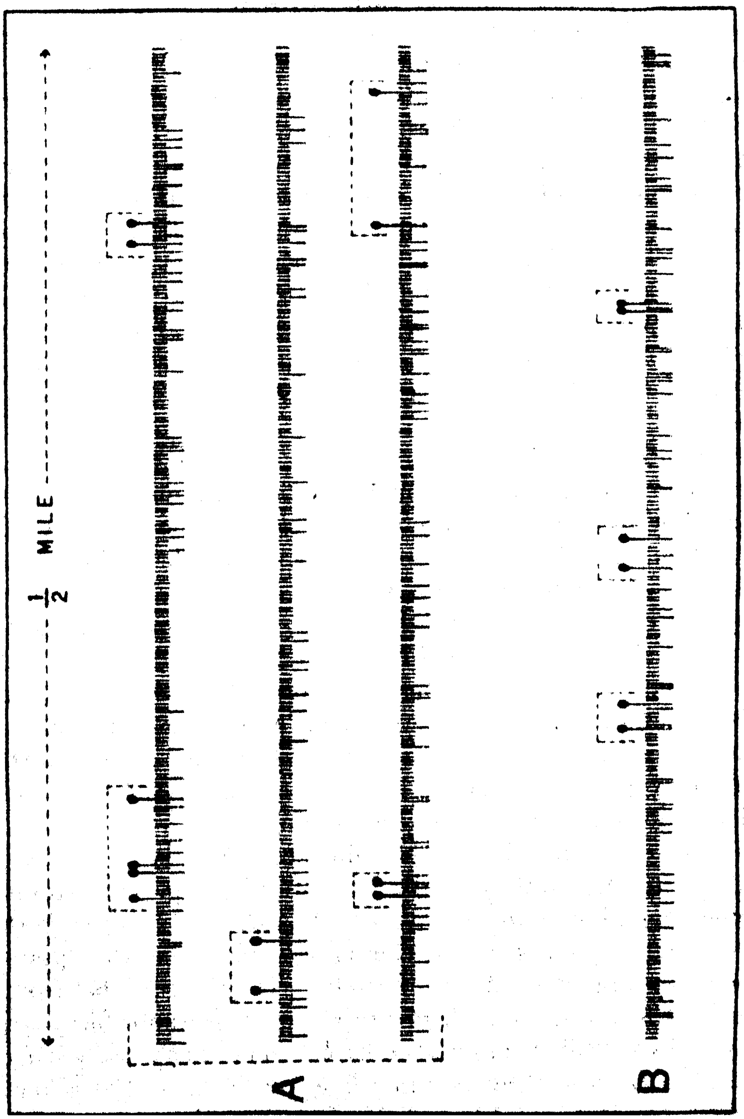


FIG. 3A.—Diagrammatic representation of the distribution of *R. montagui* and other fishes on a continuous stretch of 1½ miles of long-line—July 22, 1931.

FIG. 3B.—Distribution of *R. montagui* on ½ mile of long-line—July 23, 1931. For explanation see text, p. 224.

for the winter. Unfortunately he gives no actual data as to depths. At the western entrance to the English Channel there is little evidence of such a wholesale inshore migration in summer, at any rate within the area inside the 80-fm. line. The long-liners, which

are responsible for over 50 per cent. of the total ray landings in Devon and Cornwall, fish throughout the summer months only, mainly in depths of from 60 to 80 fm., and the pre-war tendency was for the boats to go still farther offshore into ever deeper water in order to maintain the level of their catches.

Certain conditions described by Murie [3, p. 166], however, for the Thames Estuary are borne out by observations in this area. According to this author the thornback is captured in shallow water at almost all seasons, especially during its early stages. Examination of steam trawlers' fish landed on Plymouth market indicates clearly that this statement holds good for other areas also. It is the usual custom among steam trawlers on landing rays to separate them into "small" and "large" fish—the former consisting of fish under about 40 cm. across the disc and the latter of the larger ones. Among their small fish very few *R. clavata* are to be found at any season, giving an average of not more than 5 per cent. over the year. Among their larger fish, however, *R. clavata* forms about 33 per cent. of the total.

The steam trawlers fish mainly in water of from 40 to 60 fm. in depth. The ray landings of smaller vessels fishing inside the 30-fm. line, however, consist mainly of *R. clavata*, the majority of which are of small and medium size, such as would be included in the "smalls" of steam trawlers. Over 80 per cent. of the rays caught by the research vessel *Sabella* are *R. clavata*, most of them young individuals under 40 cm. in width across the disc.

The explanation seems to be that the young fish are hatched in shallow water and remain there during their early stages of growth, moving out into deeper water when they have reached a disc width of 40 cm. or over. Corroborative evidence on this point has been obtained by means of marking experiments.

Migrations, either feeding or spawning, or both, do also occur, however, among the adult thornbacks. Murie [3, p. 167] states that, "when long-lining in the Wallet (Thames Estuary), rokers were few at the beginning of the fishing season, but as the sprats came about so did the rokers multiply. They would be from 18 inches to 2 feet wide, length in proportion, and more big than small ones. As an instance of a good catch, some thirty years back (1870 ?) in the Barrow Deep one morning, on 28 lines, 190 rokers were hooked, besides several lines being lost through weight of fish on them."

It is evident that, in those areas of the Thames Estuary, the adult thornbacks appear for a time in large numbers, probably feeding on sprats—*i.e.* they show a feeding migration.

A strikingly similar inshore migration of adult thornbacks takes place every spring in the vicinity of Plymouth. Each year, usually about the middle or end of January, while herrings, pilchards, or mackerel, are still abundant, large numbers of *R. clavata* congregate in fairly shallow water—inside the 22 fm. line—around the shore to the eastward of Plymouth Sound from Yealm Point to Bigbury Bay, and give rise to the set-net fishery already referred to (p. 222).

The landings from this net fishery present certain features of great interest. The first fish to arrive (as shown by the landings—Table I) are almost entirely females—all fully grown gravid fish nearly, but not quite, ready to deposit their eggs. In a few weeks adult male fish occur in increasing numbers. Finally, landings may consist almost entirely of adult males, the females having departed and the males having taken their place. When this happens, the fishery is nearly at an end. These male fish do not remain long behind the females which have already left the area.

TABLE I

LANDINGS FROM RAY NETS

1930.	*R. clavata.*		1931.	*R. clavata.*	
	♂♂	♀♀		♂♂	♀♀
February :			January :		
20	10	192	12	2	159
21	10	198	13	—	121
24	34	199	16	2	49
March :			19	2	198
4	1	33	20	5	156
8	20	44	22	1	75
10	2	47	23	17	123
11	67	37	February :		
12	28	41	3	2	77
15	38	—	4	—	121

All the fish move off before "spawning" takes place. Although the females caught and landed all contain almost ripe ova, in scarcely any of them are egg capsules to be found.

This congregation of thornback rays around the shore from Yealm Point to Bigbury Bay, upon which the Plymouth ray net fishery depends, is therefore an inshore feeding migration of mature adult fish. There is evidence of similar brief inshore migrations in early spring at other points along the Channel coast.

Further light on the migrations of the thornback ray has been obtained from marking experiments. Although rays are only moderately plentiful in the immediate neighbourhood of Plymouth, where these experiments have been carried out, there is one small

fishing ground on which at least a few thornback rays can usually be found at all seasons. On this ground, locally known as the "Corner" (*vide* Fig. 4—hatched area), between November 28, 1930, and May 24, 1935, 538 thornbacks were captured and released again after marking. Releases on other grounds in the vicinity (Fig. 4) were: Cawsand Bay, 49; Bigbury Bay, 30; Plymouth Sound (inside breakwater), 7. Of this total of 614 releases, 203 individuals (approximately 33 per cent.) were recaptured after periods varying from 12 to 1357 days. Details of these recaptures are given in Table II.

TABLE II

DISTANCES TRAVELLED BY RECAPTURED FISH*

Place Released.	Number Released.	Stationary.	Number Recaptured and Distance travelled.		
			Up to 5 miles.	5–20 miles.	20–50 miles.
"Corner"	528	117^{256}	15^{240}	39^{334}	10^{300}
Cawsand Bay	49	2^{71}	3^{705}	5^{391}	1^{415}
Bigbury Bay	30	5^{362}	1^{179}	2^{781}	
Plymouth Sound . . .	7		1^{312}	1^{82}	
Totals	614	124^{280}	20^{311}	47^{350}	11^{311}

* Indices indicate average number of days free.

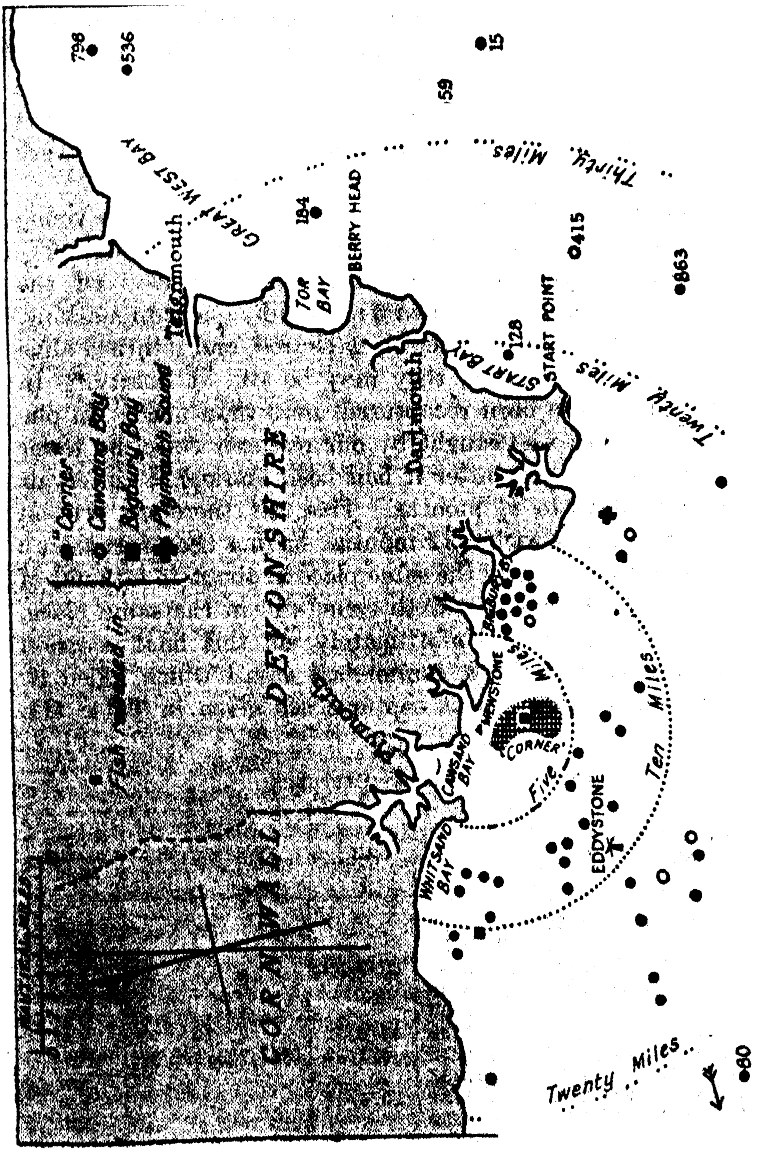
From this table it will be seen that, of the 202 fishes whose place of recapture is known, no less than 124, or approximately 61 per cent. of them, were retaken on the exact spot * where they were set free, and this in spite of the fact that the times that had elapsed between marking and recapture again varied from 12 to 1357 days. These returned fish came in at all seasons of the year, and the average period of absence was 280 days. One hundred and forty-four individuals, or 71 per cent. of the recaptures, had moved less than 5 miles, while only 11 had travelled over 20 miles. Not a single fish has as yet been returned from a distance greater than 50 miles from the point where it was set free.

In Fig. 4 are plotted the positions † of recapture of all fishes that had changed their location by more than 5 miles, the different symbols indicating place of release in each instance. The great majority of these recaptures are of fishes that were released on the

* *I.e.* as nearly as can be ascertained at sea. As the grounds in question are all close by the land, the positions were fixed with considerable accuracy by the use of landmarks on shore.

† One fish was recaptured beyond the limits of this chart at a point 22 miles farther on, in the direction indicated by the arrow.

"Corner" ground (closed circles). Six had been set at liberty in Cawsand Bay (open circles); two in Bigbury Bay (closed squares); and two just inside Plymouth Breakwater (crosses). Bearing in



of ... of marked rays that moved mo... ...hat
hav... the period of liberty (in day... dicated by ... ...tion po...
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„ 10 „ „ „ „ 30

mind that 144 fishes which had moved less than 5 miles are not plotted on it, examination of Fig. 4 shows very clearly that there is no definite migratory movement of fish from these grounds. It

must be noted, however, that most of the fish marked were immature individuals. Throughout their growing period, therefore, the young thornbacks show no migratory movement. There is simply a very slow diffusion of some fishes outwards in all directions.

Unfortunately, because of their scarcity on the inshore trawling grounds, a sufficient number of adult thornbacks has not been marked to yield useful data concerning their movements. There is evidence from other sources, however (p. 226), which suggests that a certain amount of migratory movement (probably not very extensive) is shown by the sexually mature fish.

Because of the very marked non-migratory habit of the young fish it has been found possible to capture the same individual more than once after varying intervals in the same place. Of the 150 fishes which had moved less than 5 miles subsequent to marking, 23 were recaptured by our own vessel, measured, and returned alive to the sea where, presumably, they may be still at liberty.* In addition, 10 fishes have been recaptured more than once. In one instance the same fish was caught by our research vessel no fewer than 4 times within a year after it had been marked, at intervals varying from 13 days to 4½ months. This fish, therefore, was on a ship's deck five times within 12 months, having been trawled up on each occasion from exactly the same place in about 25 fathoms of water. It was caught again a sixth time, still in the same place, 14 months after marking. Unfortunately, on this final occasion the capture was effected by a commercial vessel which killed it. Details of this and other repeat captures are given in Table III.

TABLE III

RECORDS OF REPEAT CAPTURES

Serial No.	Date Marked.	I	II	III	IV	V	Whether Released Again.
12 .	13/ 2/31	8/ 4/32	10/ 5/33				No
30 .	,,	5/ 2/32	22/ 5/32				Yes
51 .	10/10/31	8/12/31	21/12/32	29/3/33			Yes
63 .	,,	9/ 2/32	6/ 8/35				No
68 .	,,	24/ 8/32	26/ 9/33				No
133 .	23/12/31	22/ 1/32	14/ 5/32	13/9/32			Yes
226 .	25/ 4/32	22/ 5/32	25/ 8/32	5/1/33	18/1/33	1/7/33	No
285 .	12/ 5/32	29/ 7/32	7/12/32				No
1038	25/ 4/32	22/ 3/33	26/ 1/34	23/4/34			Yes
1438	12/ 5/32	15/ 7/32	2/ 8/32				No

All the fishes recorded in this table were captured and released on the "Corner" grounds in from 20 fathoms to 25 fathoms of

* The length of life of these fishes is not known.

water, and all except one were in every instance recaptured exactly where they had been originally set free. The single exception was No. 63 which, in the interval between its second and third (final) captures, had moved to Bigbury Bay. Where in this table fishes are recorded as being no longer at liberty it means that, on the final occasion of their capture, they were taken by a commercial vessel and returned dead to this laboratory. Those still at liberty were on every occasion taken by the laboratory's research vessel and returned alive to the sea after measuring.

It is important further to note that all of the fishes included in Table III—except No. 63—were immature at the time of marking and were still immature at the time of their final recapture, the largest, a female (No. 285), being then approximately 49·5 cm. in disc width. The single individual (No. 63) which, on its final capture was found to have moved a few miles away, was an adolescent female 64·5 cm. in width.

In trawling for rays for marking purposes each haul has seldom been less than 1 hour and never exceeded 2 hours in duration. That numerous fish have survived repeated capture, as recorded in Table III, indicates that they can successfully withstand pretty severe treatment. But still further, and at first rather unexpected, evidence of their capacity to withstand rough handling has been obtained. During marking operations, immediately after a catch of fish has been brought on board, the trawl frequently has been lowered again at once and the captured fish marked and released while fishing continued in progress. This became the routine method of working. In these circumstances it occasionally happens that a newly marked fish goes straight to the bottom and is caught again forthwith in the advancing trawl.* Most fishes taken twice in rapid succession in this way have survived the double capture and several have been caught again after further periods of liberty. One individual (222S), a young male 22·5 cm. in width, was caught and brought on board three times on the day of marking and, having survived, was finally released only to be taken yet again after an interval of approximately 11 months. Details of this and other repeat captures on the day of marking, and the further history of each fish, are given in Table IV. (See page 232.)

In addition, eleven other individuals were retaken once after first release on the day of marking but have not been heard of again.

* Rays returned to the sea after having been in the trawl, irrespective of whether or not they have been marked, usually swim about at the surface for a considerable time before descending to the bottom.

TABLE IV

REPEAT CAPTURES ON DAY OF MARKING

Serial No.	Details of Capture on Day of Marking.	Subsequent History.
2228 .	Retaken twice, after marking, in consecutive hauls of the trawl.	Caught again after 333 days' liberty.
2428 .	Retaken once after first release on day of marking.	Caught again after 169 days' liberty.
12 .	*Do.*	Caught again after 14 months' and 25 months' liberty (*vide* Table III).
209 .	*Do.*	Caught again after 111 days' liberty.
266 .	*Do.*	,, ,, ,, 27 ,, ,,
397 .	*Do.*	,, ,, ,, 12 ,, ,,

Three small thornbacks, however, each under 14 cm. in width, which at different times were taken in consecutive hauls, failed to recover after the second capture. Only on one occasion has a larger fish (48 cm. wide) failed to recover after two captures. This fish when it arrived on deck the second time, received a severe knock from a large stone which had found its way into the cod end, the injury so received being the probable cause of death.

These records of the survival powers of rays of different species suggest that where these fishes form an important part of the catch—as in English Channel waters—it would well repay commercial trawl-fishing vessels to take the shortest possible hauls which are consistent with fishing efficiency, and to return at once to the sea all rays that are too small to be marketable. Possibly the very smallest individuals might not recover, but the larger unmarketable sizes would almost certainly live. Being non-migratory, these young fish would remain on the same grounds until they reached saleable size; they would not move away to another area where other fishermen (perhaps less careful of their own stocks) would reap the benefit. The non-migratory habit of these fishes in their growing stages, coupled with a relatively long juvenile life (*vide* p. 233–4 *infra*) is also important in that it increases the possibility of reducing the stock on any particular fishing ground by too intensive fishing. Unlike migratory species which are exposed to capture only for so long as they remain in a fishable area, and whose numbers tend to be sustained or replenished by immigrants from other localities, the rays present on fishable ground remain constantly exposed to capture, and their numbers will be augmented only very slowly by gradual infiltration of individuals from adjacent regions where fishing is impossible or less intense.

Growth

Of the 202 recaptured fish whose place of recapture is known, figures relating to size have been received for 197 of them. Ten of these have been captured more than once and more than one record of growth has been obtained.

In Table V the mean growth increments grouped at monthly intervals for fishes of 10-cm. size groups are given, the indices denoting the numbers of fish upon which the entries are based. Only 2 fishes of the very smallest size group (10–19·5 cm.) have been returned. It would seem that many of these very small individuals do not survive the ordeal of marking, although returned to the sea in very vigorous condition. Notwithstanding that the smaller of the two marks in use is invariably affixed to them, it is relatively an enormous encumbrance to such tiny fishes, not to mention the relative severity of the operation when placing it in position. The use of a still smaller mark is impracticable.

At the other end of the scale, only very few fishes over 60 cm. disc width have been marked, and only one returned. As mentioned above, most of the fishes present on the Plymouth grounds are immature individuals and it is therefore mainly to those sizes, from about 20 cm. to 50 cm. disc width, that the data so far collected apply.

Examination of Table V shows that, over this range—although there is considerable variation in the data owing to individual differences in growth-rate—a growth increment of from 4 cm. to 8 cm. in width of disc takes place in a full year. (See page 234.)

The rate of growth of both sexes is approximately the same over the size range represented. For reasons already stated no data are available from marking experiments on the growth rates of the largest size groups. Observations on market categories [7, pp. 890 *et seq.*], however, reveal that in the males first-maturity is reached at or shortly after a disc width of 50 cm. is attained, and that thereafter their growth rate rapidly falls off. Male thornbacks seldom exceed and usually fail to reach 60 cm. disc width.

The females, on the other hand, do not reach first-maturity until they have attained a disc width of from 65 to 70 cm., and old adults of over 80 cm. disc width are not uncommon. Since both sexes grow at about the same rate until the male reaches first-maturity it follows that the males become adult at a younger age than the females. Thornback rays hatch out from the egg having an average disc width of approximately 8 cm. [5, p. 595]. Taking 6·0 cm. per annum as an average growth rate in both sexes until the onset of

TABLE V

Mean Size Increments of Marked *Raia clavata*

Grouped at monthly (= 4-weekly) intervals. Size increments in cm. Indices denote numbers of fish upon which entries are based when more than one.

Months at Liberty.	Size group (cm.).												
	10–19·5		20–29·5		30–39·5		40–49·5		50–59·5		60–69·5		
	♂	♀	♂	♀	♂	♀	♂	♀	♂	♀	♂	♀	
0 .			$0{\cdot}17^{6}$	$0{\cdot}0^{4}$	$0{\cdot}3^{2}$	$0{\cdot}0^{4}$	$0{\cdot}0^{2}$	$0{\cdot}2^{3}$	$0{\cdot}5^{2}$	0·0			
1 .				$0{\cdot}1^{4}$	$0{\cdot}5^{5}$				$1{\cdot}3^{2}$	0·0			
2 .			0·5	0·5	$2{\cdot}3^{2}$	$1{\cdot}2^{2}$	0·5			$0{\cdot}3^{2}$		0·5	
3 .			$1{\cdot}2^{3}$		$2{\cdot}0^{3}$	$1{\cdot}2^{3}$	$0{\cdot}5^{2}$		0·0	2·0			
4 .			$2{\cdot}0^{2}$		$1{\cdot}5^{2}$	$1{\cdot}8^{3}$	1·0	$0{\cdot}5^{3}$		1·0			
5 .					0·5	1·0	3·0			$2{\cdot}0^{2}$			
6 .			0·0	3·0	$3{\cdot}1^{3}$	3·0		0·5	2·0	$3{\cdot}0^{2}$			
7 .				1·5	$2{\cdot}5^{2}$	$4{\cdot}2^{3}$	$3{\cdot}8^{2}$	3·5					1 year.
8 .			$3{\cdot}3^{2}$		3·5		2·5	$3{\cdot}0^{2}$					
9 .			6·0	4·5	5·0	- $3{\cdot}3^{3}$		$5{\cdot}2^{3}$	0·5				
10 .			5·0			4·5		5·5	3·5	6·5			
11 .			2·5		3·5	$3{\cdot}0^{2}$	3·0	6·5	5·0				
12 .				4·5	8·0	3·0							
13 .			5·5				$5{\cdot}5^{2}$						
14 .			$7{\cdot}3^{2}$			$4{\cdot}5^{2}$		6·5		9			
15 .		5·5			7·5	$7{\cdot}3^{2}$	5·5		5·5				
16 .					9·0	11·5				$3{\cdot}8^{2}$			
17 .			$8{\cdot}3^{2}$		5·5	$7{\cdot}0^{2}$							
18 .			8·0					8·0					
19 .					$9{\cdot}8^{3}$	16·0	7·5	9·5					
20 .					7·5					11·5			2 years
21 .						4·5	$10{\cdot}5^{2}$	6·0					
22 .							5·5						
23 .					4·5								
24 .							5·5						
25 .			17·0		12·0								
26 .				16·0									
27 .										18·0			
28 .								13·0					
30 .						17·5							
31 .							$7{\cdot}8^{2}$						
33 .	7·5												3 years.
34 .						6·5	12·5			11·5			
36 .						16·5	12·0						
39 .				13·0									
43 .						31·0							
45 .			28·0				9·0						4 years.
48 .				$29{\cdot}5^{2}$									
52 .													

sexual maturity, it follows that the males reach this stage when they are about 7 years of age whereas the females do not become sexually mature for another 2 years or so.

Food and Feeding

Of the foraging habits of the Raiidæ little is known. It is

nevertheless certain that they depend upon "scent"—or at any rate some sense other than sight—for the finding and recognition of their food or prey. For in long-line fishing, where the catch depends upon the fish finding and taking the bait, there is no difference at all in the magnitude of day and night hauls. Neither the brightest day nor the darkest night appreciably affects the catches of ray. They thus differ markedly from turbot which, being sight feeders, are seldom caught in any number on lines during the night, but are readily taken by day.

As is already well known, young rays feed very largely upon small crustaceans, especially Amphipods and Crangonids [5, p. 635]. In the vicinity of Plymouth the Amphipod *Ampelisca spinipes* is of primary importance, being present in large numbers on certain grounds [6, p. 681]. As the fish increase in size they turn their attention to larger crustacea such as Upogebia, Portunus, and Corystes, and—in certain species at least—to fish. Adult thornbacks, in fact, sometimes feed entirely on fish. The large rays of this species taken by the nets already mentioned (p. 227) were in both 1930 and 1931 found to be feeding exclusively on herrings and sprats. Of several hundreds of stomachs examined, not one was found to contain anything but fish, mainly herring (sometimes as many as six in one stomach), and not more than half a dozen empty stomachs were encountered. Several large *R. Brachyura* and a few large *R. batis* taken in the same locality also had their stomachs full of herrings. One of the latter, a female measuring 143 cm. across the disc, contained no less than nine large fish.

Other fish, commonly including rays, also enter largely into the diet of adult *Raia batis*. Of 41 stomachs of these fishes, ranging from 89 cm. upwards in width of disc, that I have at various times examined, 13 contained one or more Raia sp. Those specimens of which the species could be determined consisted of *R. nævus* and *R. montagui*, with one doubtful *R. clavata* among them.

The Toll of a Fishery

During the period between the two great wars there was an alarming decrease in the landings of rays and skates from the English Channel area. Certain factors, external to the fishery itself, helped, in some years at least, to bring about this decline. But that it reflected a real change in the available stock of fish was clearly indicated by events and conditions in the Cornish section of the industry.

Before the outbreak of the 1914–18 war and for a few years after its close the Cornish long-line fleet, working from Newlyn,

used on an average to work from 1000 to 1500 hooks per vessel on from 2½ to 3 miles of line. Gradually they became obliged to use from 2000 to 4000 hooks on from 5 to 7 miles of line in order to catch the same amount of fish or rather less. Moreover, instead of fishing as a rule within a radius of 50 miles from the port they had to operate on grounds up to 90 or even 100 miles distant. In due course no further increase in the amount of gear that could be used from the existing vessels could be made. The extreme limit of their range was also reached, and the catches continued to fall. It is doubtful whether the introduction of larger vessels capable of working more gear and going farther away from port would have arrested this decline other than temporarily. In fact, such developments in all probability would have hastened the decline. But war came and the grounds were rested, and catches are good once more. But with such slow-growing fishes, that are also demersal and non-migratory in their young stages, it seems certain that overfishing will soon cause renewed depletion of the stocks, especially if trawling is carried out as intensively as before.

In this connection it is important to emphasize that in line fishing, unlike trawling, there is a complete absence of any destruction of non-marketable small fish. Should the question ever arise in a restricted area of devising means for the preservation of a skate and ray fishery, a useful preliminary step would be to consider the possibility of substituting lining for other more destructive methods of fishing.

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THE TOXICITY AND PROPERTIES OF THE GLYCOLS

By ETHEL BROWNING, M.D.

THE potential toxicity of any solvent used in industry can usually be estimated only by experiment, either human or animal; its actual toxicity is too often established by accident, with results which may be serious or even fatal. This latter method of estimation occurred with two members of the group of solvents known as the glycols and their derivatives—diethylene glycol and diethylene dioxide, or dioxan. In the case of diethylene glycol the accident was non-industrial, following its use in America as a vehicle for an "elixir of sulphanilamide"; in the case of dioxan, an alteration in an experimental textile plant leading to a higher concentration of the vapour was followed by the death of five men who had worked in apparent safety on the same process for sixteen months. Until this disaster, which occured in 1933, relatively few animal experiments on this particular group of solvents had been carried out, and those which had been made on dioxan itself had appeared to place it low in the order of toxicity. This is an instance of the difficulty, often encountered, of translating the results of animal experiment in terms of toxicity to human beings. Of recent years efforts have been made in many instances to correlate as far as possible the experimental environmental conditions with those actually encountered in industry, with the result that the toxicity, both potential and actual, of many solvents, including the glycol group, is now well defined and clearly understood.

INDUSTRIAL USES OF THE GLYCOL GROUP

Glycols and their derivatives, the ethers and esters, have many and varied applications in industry, and are becoming of increasing importance, since many of them are good solvents for lacquer. Among their other applications are their use as anti-freeze mixtures, vehicles for flavouring essences, pharmaceutical preparations and cosmetics, in the textile industry, as an intermediate in the synthetic rubber industry and, especially in America, for the "stiffening" of shirt collars and "cooling" of cigarette tobacco. Of recent years, apart from their use as solvents, ethylene and propylene glycol have

been employed as air sterilising agents. It is obvious that the full knowledge of the nature and degree of any hazard attached to their use in so wide a field should be available.

Properties.—Upon the volatility of the different members of the group depends largely the degree of toxicity, from the industrial point of view, of the individual substance.

The glycols themselves—ethylene, diethylene, butylene and propylene—are volatile only with difficulty. Ethylene glycol, for example, is 2625 times less volatile than ether.

The ethers—ethylene glycol monoethyl ether (methyl cellosolve), mono-methyl ether (cellosolve), mono-*n*-butyl ether (butyl cellosolve), the mono-ethyl and mono-*n*-butyl ethers of diethylene glycol, dioxan, and diethylene oxide (tetrahydrofuran)—are of high volatility, while the ether esters—ethylene glycol monoethyl ether monoacetate (cellosolve) acetate and diethylene glycol monoacetate—occupy an intermediate position.

The boiling point is another important factor in their industrial application. Ethylene glycol itself, with a B.P. of 191 to 200° C., and its diacetate with a B.P. of 186 to 190° C., are unsuitable as solvents for lacquer, while the monomethyl ether (methyl cellosolve) with a B.P. of 124 to 125° C. and the monoethyl ether (cellosolve) B.P. 126 to 138° C., are widely used in the lacquer industry.

Toxicity.—All members of the glycol group are injurious to the kidneys, and many to the liver, if allowed to enter the blood stream in sufficiently high dosage. In the case of those of low volatility, such high dosage can only be attained by ingestion, either accidental, or as the result of being used as pharmaceutical vehicles. Accidental ingestion of anti-freeze radiator fluid has very recently (1946) been responsible for eighteen fatal cases in America, while the disastrous results of diethylene glycol used as an "elixir" has already been mentioned. A comparison of the toxicity to animals of several of the glycols used as constituents of food and drug preparations made by Laug, Calvery, Morris and Woodward in 1939, using the method of introduction by stomach tube, led them to conclude that all except propylene glycol should be omitted entirely from food and drug preparations.

The danger of acute poisoning from inhalation is greatest, naturally, with the highly volatile ethers, and, though with care in the normal conditions of their industrial use this should not occur, serious trouble has arisen in exceptional circumstances. Such exceptional circumstances were present in the five fatal cases of dioxan poisoning, where an unusual and unforeseen extent of exposure took place.

The lesions of the kidneys, which in animals are degenerative in character, and which in the fatal cases examined at autopsy have shown themselves as a symmetrical necrosis of the cortex, sometimes as a deposition of crystals of calcium oxalate, were for some time attributed to the production in the body of oxalic acid as a metabolite of some of the glycols. This hypothesis seemed to be supported by the finding of Hanzlik, Seidenfeld and Johnson (1931) that daily doses of 2·2 gm. per kg. of ethylene glycol to animals gave rise to oxaluria and renal calculi. Later investigations of a number of the glycols by Wiley, Hueper *et al.* (1938), however, showed that, while some of these substances, notably ethylene glycol itself, did increase the urinary oxalic acid, the amount was scarcely sufficient to explain their toxicity. It is now thought by many investigators that the toxic action may be due to other toxic intermediates that are destroyed within the body, and that the high incidence of casts in the pyramidal tissue may indicate the existence of some local disturbance of the calcium metabolism. A more extended series of investigations by Morris, Nelson and Calvery in 1942, in which animals were fed at levels of 1–4·9 per cent. of various glycols (according to their equimolecular concentrations) for two years, revealed the presence of actual laminated mulberry bladder calculi. With some glycols these stones contained approximately 80 per cent. of calcium oxalate.

The presence of degenerative changes in the testes and brain of experimental animals given daily injections of ethylene glycol was regarded as evidence of systemic organic injury by the injected substance. Testicular enlargement, œdema and tubular atrophy have been observed, especially in animals fed for two years on ethylene glycol monoethyl ether.

The narcotic action of the glycols as a group is not high; tetrahydrofuran has the most definite action in this respect, inhalation of 400 mg. per litre producing deep narcosis in animals.

Their irritant action on skin and mucous membranes is also not high, solutions of 20 per cent. producing only slight reddening of the human skin, though injection of solutions of this strength of ethylene glycol and diethylene glycol monoethyl ether into the abdomen of guinea pigs caused extensive infiltration and tissue necrosis (Walther, 1942). Some members of the group are slightly irritating to the nose and throat when inhaled, and dioxan and tetrahydrofuran cause inflammation of the respiratory tract.

Relative Acute Toxicity.—The toxicity of various members of the series in relation to each other has been determined by animal experiments which are not completely uniform, since various species

were used by different investigators and various methods of administration.

One series, for example, examined by von Oettingen and Jirouch, (1931) by subcutaneous injection into mice, indicated that the lethal toxicity in decreasing order of the glycol products investigated was as follows:

> ethylene glycol mono-*n*-butyl ether (butyl cellosolve); ethylene glycol; diethylene glycol; ethylene glycol monoethyl ether (cellosolve); diethylene glycol monoethyl ether (carbitol); ethylene glycol monoethyl ether monoacetate (cellosolve acetate); dioxan.

Examination of another series by Laug *et al.* (1939), by stomach tube introduction, on the basis of L.D.50,* gave the following results (also in decreasing order):

> ethylene glycol monoethyl ether (cellosolve); dioxan; diethylene glycol monoethyl ether (carbitol); ethylene glycol; diethylene glycol; propylene glycol.

By inhalation, the relative acute toxicity has not been closely correlated, but some experiments quoted by Lehmann and Flury (1943) appear to indicate that of the more volatile glycol derivatives, cellosolve and methyl cellosolve are the most toxic, followed by dioxan and tetrahydrofuran. Butyl cellosolve, ethylene glycol monoacetate (solvent G.C.) and ethylene glycol monomethyl ether (methyl cellosolve acetate) were relatively well tolerated even in saturation concentrations.

(In this relation it is interesting to note that the ideal concentration of ethylene and propylene glycol suggested for air sterilisation is just below saturation, and this advocacy is supported by the demonstration of Robertson (1942) that rats and monkeys maintained for a year or more in atmospheres saturated with the vapours of propylene and triethyleneglycol could thrive and bear young.)

From all investigations it appears that propylene glycol is the least toxic of the group; butylene glycol and its methyl acetate are practically non-toxic; the "cellosolve" varieties (cellosolve, methyl cellosolve, butyl cellosolve, and cellosolve acetate) are among the most toxic.

* L.D.50 means the lethal dose for 50 per cent. of the experimental animals.

The Individual Members of the Group

ETHYLENE GLYCOL

Ethylene glycol is a colourless, odourless, somewhat viscous and hygroscopic liquid, non-inflammable, but evolving heat when mixed with water. It has a B.P. of 191–200° C., and is of low volatility (2625 times less volatile than ether).

Its chief applications in industry are:

(1) As a constituent of anti-freeze mixtures for car radiators.
(2) As a constituent of cosmetics and flavouring essences.
(3) As a constituent of ethylene glycol electrolyte for electrolytic condensers.
(4) As a solvent for pigments, *e.g.* for printing textiles.

Toxicity

From the industrial point of view, the use of ethylene glycol does not appear to be attended by any great danger to health, since absorption by inhalation is unlikely to occur, owing to its slight volatility, and there is no evidence of absorption through the skin. Acute poisoning by ingestion, with fatal results, has occurred, and the minimal lethal dose for human beings is estimated at about 100 c.c.

Toxicity to Animals

(*a*) *Acute.*—In large doses, by feeding or injection, ethylene glycol acts as a poison to the central nervous system and to the kidneys. The symptoms preceding death, and following an ingested dose of 5–13 c.c. per kg. or an intravenous injection of 2·5–4·5 c.c. per kg. were those of loss of equilibrium, general motor depression and in some cases twitchings, tremors and convulsions. The injury to the kidneys consisted of degenerative lesions (nephrosis) with a high incidence of calcium casts in the pyramidal tissue.

Inhalation of concentrations of 0·5 mg. per litre (approximately the saturation value) produced only slight narcosis, with complete recovery.

(*b*) *Chronic.*—Small amounts, given orally or subcutaneously, caused no injury to the kidneys, but daily feeding doses of 2·2 gm. per kg. or injections of 5 c.c. were followed by degenerative lesions in the kidneys, in the spermatogenic epithelium of the testes and of the ganglion cells of the brain. These doses also produced oxaluria and renal calculi, while feeding at levels of 1–2 per cent. of the diet for periods of two years produced, in the experiments of Morris *et al.* (1942), actual laminated mulberry stones in the bladder.

Inhalation of the order of 300 mg. per 1000 litres of air produced no significant pathological changes.

Toxicity in Man

(*a*) *Acute.*—The most recent of the fatal cases which have occurred following the accidental ingestion of ethylene glycol have been described by Pons and Custer (1946). In only one of these eighteen cases was the approximate amount taken known—200 c.c. of an anti-freeze mixture.

Death appears to have been due to respiratory failure, following vomiting, convulsions and coma within the first few hours. In these cases the urine contained oxalate crystals, which were also present in the kidneys, but only one case showed severe damage to the renal epithelium. Lesions in the central nervous system varied from congestion and œdema to exudative meningo-encephalitis. In one of two similar non-fatal cases (Hansen, 1930; Brekke, 1930), however, when death was apparently averted by surgical decapsulation of one kidney, a condition of hæmorrhagic nephritis was found.

(*b*) *Chronic.*—Symptoms of chronic intoxication from industrial exposure to ethylene glycol have been practically non-existent, but slight urinary abnormalities, albuminuria and a few red blood corpuscles were found during an investigation by the Factory Department (Browning, 1937).

Ethylene Glycol Monoethyl Ether (Cellosolve) (Ethyl Glycol)

A colourless liquid with a slight odour. Boiling range 126–138° C. It is a powerful solvent for nitrocellulose, and its chief industrial application is in the lacquer industry. Its volatility is considerably higher than that of ethylene glycol—43 times less volatile than ether.

Toxicity to Animals

(*a*) *Acute.*—The toxicity of ethyl glycol relative to that of other members of the group, as assessed by animal experiment, appears to differ according to the method of introduction. By stomach tube, according to Laug *et al.*, it is the most toxic of those examined; by subcutaneous injection, according to Walther (1942), it is slightly less toxic than ethylene glycol itself.

By inhalation, the toxicity appears to be low; in Waite, Patty and Yant's experiments (1930) it required 24 hours' continuous exposure to 0·6 per cent. by volume of the vapour (approximately saturated mixture) at room temperature to kill the animals during the time of exposure, or a similar exposure to half-saturated air to kill them 24 hours after removal from exposure.

The effect on the central nervous system was less than that of many other ethylene glycol derivatives, a fact which has been attributed to its slight effect in precipitating protein (owing to its relatively high surface tension) and its low lipoid partition coefficient. On the kidneys, the effect of large doses by injection or by stomach tube is that of acute nephrosis.

(*b*) *Chronic.*—Oral administration of 0·1 to 2·0 c.c. per kg. daily to rabbits produced, according to Flury and Zernik, evidence of kidney injury, and subcutaneous injection of 0·5 c.c. per kg. had the same effect, some animals dying after the seventh injection. Testicular lesions (interstitial œdema and tubular atrophy) were more marked with this substance than any other in the long-term feeding experiments of Morris, Nelson and Calvery (1942). Inhalation of 0·14 vols. per cent. for 8 hours daily had variable results, but cats died after 4–5 days, the kidneys showing glomerulitis.

Toxicity in Man

No definite symptoms of intoxication from the industrial use of ethyl glycol have been reported.

Ethylene Glycol Monomethyl Ether (Methyl Cellosolve, Methyl Glycol)

A colourless liquid with a faintly alcoholic odour. Boiling range 124–125° C. Volatility 34·5 times less volatile than ether. It is a good solvent for cellulose acetate and nitrate, and is used in the lacquer industry, especially for white lacquer. It is also used to some extent in America as a solvent for rotogravure inks, in the manufacture of adhesives, and as a stiffener for "fused" collars.

Toxicity to Animals

(*a*) *Acute.*—By subcutaneous injection, methyl cellosolve appears to have a relatively high toxicity, about 2 c.c. proving fatal to rabbits, with signs of injury to the kidneys.

Inhalation of an almost saturated mixture (Flury and Zernik, 1931) (0·93 vols. per cent.) proved fatal to some guinea pigs, but cats and rabbits recovered.

(*b*) *Chronic.*—Repeated feeding of 1–2 c.c. per kg. proved fatal to rabbits. After repeated subcutaneous injection of 0·5–1 c.c. per kg. to guinea pigs and 1 c.c. to rabbits (Flury and Zernik, 1931), albumen, red blood cells and cylinders were present in the urine.

Inhalations of 0·08–0·16 vols. per cent. had variable results, some animals dying after 10–12 days, all showing evidence of

Toxicity in Man

So far no evidence of kidney injury from the use of methyl cellosolve in industry has been reported, but three cases of "toxic encephalopathy," indicating an effect on the central nervous system, have been described, all in the shirt collar industry (Donley, 1936, and Parsons and Parsons, 1938). A further examination of nineteen workers in the same factory by Greenburg *et al.* (1938) revealed several slighter cases of neurological and mental abnormality.

In the two most severe cases (Parsons and Parsons)—young men employed in dipping shirt collars in a fluid containing methyl cellosolve—the most outstanding symptom was a change of personality, from intelligence and quickness to stupidity and lethargy. This was accompanied by lassitude, sleepiness, giddiness, severe frontal headache, burning and weakness of the eyes, persistent dilatation and sluggish reaction to light and accommodation of the pupils, general hypertonicity of skeletal muscles, hyperactivity of all reflexes, moderate ataxia and a positive Rhomberg sign. Both men showed loss of weight and some nocturia, and a moderately severe anæmia with a high colour index and granulopenia. Both recovered, with apparently no permanent damage.

Of the other nineteen workers examined at a later date, four showed the same type of mental retardation, and four others abnormal nervous reflexes and tremor of the hands, while anæmia of a macrocytic type was present in eight cases.

A method of estimation of the atmospheric concentration of methyl cellosolve has been described by Elkins *et al.* (1942), using the differential oxidation by potassium dichromate. The actual concentrations in the factory referred to above were 25 parts per million with the windows open, 76 with the windows closed.

Greenburg *et al.* suggest 25 p.p.m. as the maximum safe concentration for methyl cellosolve.

Ethylene Glycol Monoethyl Ether Monoacetate (Cellosolve Acetate)

A colourless liquid with an ester-like odour. Boiling range 140–160° C. Volatility—52 times less volatile than ether. A good solvent for nitrocellulose, cellulose ether and some resins. It is used chiefly in the lacquer industry.

Toxicity to Animals

(*a*) *Acute.*—By subcutaneous and intravenous injection cellosolve acetate appears to have about the same lethal toxicity as methyl cellosolve. It has a paralysing effect on the central nervous

system and a stronger depressant action on skeletal and smooth muscle than any other of the glycol derivatives examined, except butyl cellosolve. Subcutaneous injection of large doses produces acute nephrotic lesions in the kidneys.

Inhalation of approximately saturated air mixtures (20 mg. per litre) or of "mists" of 21–54 mg. per litre produced neither serious systemic effects nor abnormal urinary findings, but cats inhaling 55 mg. per litre developed paralysis, cramps, and albuminuria, and died after 24 hours (Flury and Zernik, 1931).

(*b*) *Chronic.*—Repeated injections or inhalations appear to be fairly well tolerated by animals. Dogs given subcutaneous injections of 8·5 c.c. daily by Wiley, Hueper *et al.* (1938) showed no symptoms of toxicity, but those killed some days after the last injection showed some calcium casts, mild nephrotic lesions and some degenerative lesions of the testes and brain. Some increase in urinary oxalic acid was found, as in the case of ethylene glycol, but not enough to account for the lesions found (Flury and Zernik). Inhalation of 2·5 mg. per litre for 8 hours daily also produced no toxic symptoms, though some animals died after 6–9 days, with urinary abnormalities and signs of kidney injury.

Toxicity to Man

No injury from the industrial use of cellosolve acetate has been recorded.

Ethylene Glycol Mono-n-Butyl Ether (Butyl Cellosolve) (Butyl Glycol)

A colourless liquid with a mildly rancid odour. Boiling range 164–182° C.

A good but slow solvent for cellulose nitrate and some resins. It is used in the lacquer industry for brushing lacquers and for reducing the viscosity of lacquers, and also in the textile industry as a constituent of the "wetting out" solution.

Toxicity to Animals

(*a*) *Acute.*—As estimated by subcutaneous injection, butyl cellosolve appears to be the most toxic of all the glycol derivatives, with a rapid paralytic action on the central nervous system. It has also a strong paralysing effect on sensory nerve endings which can be experienced by tasting some of the liquid, a burning sensation followed by numbness of the tongue being produced.

Its action on the kidneys is also highly toxic, marked hæmorrhagic and nephrotic changes being produced by the injection of 12·5 c.c.

per kg. body weight of a 50 per cent. aqueous solution (von Oettingen and Jirouch, 1931).

Inhalation, however, appears to be well tolerated; according to Flury and Zernik (1931) concentrations of 10 mg. per litre caused only mucous membrane irritation, with no after-effects.

(*b*) *Chronic.*—Repeated inhalations of 2·5–5 mg. per litre daily was relatively non-toxic, but a few animals that died showed injuries of the kidneys and liver.

Toxicity to Man

Only one case of possible kidney injury has been reported with hæmaturia, and casts in the urine, but the exposure of the man in question was not definitely exclusively to butyl cellosolve, and a month later the urine showed no abnormality (Browning, 1937).

ETHYLENE GLYCOL DIETHYL ETHER (DIETHYL CELLOSOLVE)

A colourless liquid, B.P. 121° C., which is not very soluble in water and is a good solvent for cellulose nitrate and some resins. Volatility 29·2 times less volatile than ether. It is used, but not widely, in the lacquer industry. From animal experiments it appears to have a narcotic effect in high dosage, but injection of 9·5 c.c. daily into dogs (Wiley, Hueper *et al.*, 1938) produced no symptoms of intoxication and no increased urinary oxalic acid.

Degenerative lesions of the kidneys and a mild degree of degeneration of liver cells and brain tissue were found at autopsy in dogs killed, and in rabbits generalised atrophy of the testes also. Though well tolerated by inhalation with repeated dosage, definite signs of kidney injury were found after death.

ETHYLENE GLYCOL MONOACETATE (SOLVENT G.C.)

An odourless, colourless liquid, miscible with water or aromatic hydrocarbons. B.R., 185–195° C. (606 times less volatile than ether). Its low volatility gives it only a limited application in the lacquer industry; it is more widely used in the textile industry, for printing on fabrics, also in the manufacture of essences and cosmetics.

Toxicity

Animal experiments by the subcutaneous route have shown the monoacetate to have very much the same effect and toxicity as ethylene glycol. Injections of 8·5 c.c. daily to dogs, while producing no actual symptoms of toxicity, did produce degenerative lesions of the kidneys, testes and brain. It has also about the same effect as ethylene glycol in causing an increase in the urinary excretion of oxalic acid.

DIETHYLENE GLYCOL

A colourless, odourless liquid, more viscous and more hygroscopic than ethylene glycol. B.P. 244·5° C. It is used to some extent in the lacquer industry and was used (with the disastrous results described above) at one time as a vehicle for medicinal preparations. It has also been used as a substitute for glycerine as a hygroscopic or "cooling" agent for cigarettes.

Toxicity to Animals

Both the acute and the chronic toxicity of diethylene glycol appear to be slightly less than that of ethylene glycol. It has, however, the same deleterious effects on the lower urinary tract with prolonged administration by mouth, producing large laminated oxalate calculi in the bladder, but the chronic cystitis accompanying them was less than with ethylene glycol.

In some recent (1946) investigations by Fitzhugh and Nelson it produced in 4 per cent. concentration also bladder tumours, showing varying degrees of malignancy, hydronephrotic changes in the kidneys and moderate liver damage.

Toxicity to Man

The fatal effects of diethylene glycol when ingested have already been mentioned. In 1937, 60 deaths occurred in America as the result of drinking a sulphanilimide-elixir containing about 72 vols. per cent. of diethylene glycol. The symptoms were drowsiness, pallor, slight œdema of the face, scanty urine with albuminuria or anuria; later œdema, ascites and coma.

No effects from its inhalation have been observed. When inhaled in the smoke of cigarettes to which it has been added, it does not appear to have given rise to any symptoms, not even so much irritation of the throat as caused by glycerine (Flinn, 1935).

DIETHYLENE DIOXIDE (DIOXAN)

Dioxan is an anhydrous, colourless liquid with a faint odour like that of butyl alcohol. B.R. of the technical substance 94–111° C., of the pure product 101·1° C. Its volatility lies about midway between the highest and lowest of the glycol group (4·3 times less volatile than ether). It is used in the textile industry (for treating artificial silk yarn); in the lacquer and celluloid industries; as a paint remover, as a degreaser, especially for wool; as a preservative, fumigant or deodorant, and in the manufacture of pharmaceuticals and cosmetics.

Toxicity to Animals

The effects of subcutaneous, intraperitoneal and intragastric administration to animals do not appear to be similar to those of inhalation, though even by this route the effects are relatively slight unless high concentrations or long exposure or both are used.

On the basis of subcutaneous injection the toxicity of dioxan is relatively very low compared with other glycols tested by the same method. Although the lesions found in animals killed after injection included degenerative changes of the cortical tubules of the kidney and calcified debris in the pyramidal tubules, these effects do not appear to be due to the formation of oxalic acid, since none of the animals showed any increase in urinary oxalic acid excretion (Wiley, Hueper *et al.*, 1938).

By inhalation, the results show a striking difference according to the length of exposure. In an investigation by Yant and co-workers in America in 1930, single exposures of 3 hours or more to 3 per cent. concentration were used. These produced narcosis and finally respiratory failure, but lesions of the kidneys or liver were not significant. In the investigations by Fairley *et al.* in England in 1933–4, lower, non-lethal concentrations (1 in 500 and 1 in 1000) were used over long periods, and marked changes were found in kidneys and liver.

By inhalation also dioxan has a marked irritative effect on mucous membranes, conjunctival, gastric and pulmonary. Though producing no irritation of the skin, it can be absorbed by the skin, lesions of the kidneys having been observed in animals after application.

Toxicity to Man

The five fatal cases among workers in an artificial silk factory which occurred in 1933 have apparently been the only instances of industrial injury by dioxan, and it is now known that the exposure had been exceptionally high for two months before the onset of symptoms. All five died, with anuria, uræmia and coma, within a fortnight of the appearance of symptoms of "stomach trouble," and it was later found that others of the 80 men employed had suffered from similar gastric disturbance. Though none had shown jaundice, it has been suggested (Estler, 1935) that these early symptoms were an indication of the liver involvement subsequently revealed at autopsy.

These lesions of the liver were characteristically unlike the fatty degeneration or yellow atrophy found with other liver poisons, such

as alcohol or chloroform; they consisted of acute necrosis of the inner half, or often two-thirds, of each lobule.

The kidneys showed a very acute hæmorrhagic nephritis. Whether these fatalities were due to severe chronic poisoning, a slow cumulative effect brought to a climax by the two months' unusually heavy exposure, or whether they were due to acute poisoning by repeated short, heavy exposures is not clear, but some authorities have stressed the "unsuspected and insidious long range effect."

TETRAHYDROFURAN (DIETHYLENE OXIDE)

A colourless liquid of etheric odour miscible with water and alcohol, soluble to some extent in olive oil. Its volatility is relatively higher than that of dioxan (2·8 times less volatile than ether). It is used chiefly as a solvent for lacquer, and has been suggested for use in destroying the apple moth.

Toxicity to Animals

Tetrahydrofuran is the most highly narcotic of the glycol derivatives, producing a moderately severe irritation of skin and mucous membranes, and in fatal doses has an injurious effect on the kidneys.

Acute Toxicity.—The fatal dose by ingestion in rabbits is about the same as that of ethylene glycol, but smaller doses cause narcotic symptoms and irritation of the gastric and intestinal membranes, as well as injury to the kidneys and liver. Inhalation of 50 mg./l. (1·7 per cent.) caused marked narcosis and most of the experimental animals died after a single inhalation of 400 mg./l.

Chronic Toxicity.—Considerable injury to the kidneys was caused by repeated inhalation of 10 mg./l. (Lehmann and Flury, 1943).

DIETHYLENE GLYCOL MONOETHYL ETHER (CARBITOL)

A colourless hygroscopic liquid, miscible with water. B.R., technical product 150–200° C.; pure 198° C. It is a good solvent for cellulose nitrate and is of relatively low volatility (907 times less volatile than ether). It is used chiefly in the textile industry and in dye printing.

Toxicity to Animals

By subcutaneous injection carbitol appears to have about the same toxicity as diethylene glycol and cellosolve; slightly less than ethylene glycol.

Inhalation is well tolerated; Lehmann and Flury (1943) observed no injury to animals inhaling almost saturated concentrations for 12 days.

Large doses of carbitol produce the same degenerative and nephrotic effects on the kidneys of animals as other glycol derivatives. No injury to human beings has yet been reported.

Diethylene Glycol Mono-*n*-Butyl Ether (Butyl Carbitol)

A colourless liquid of mild odour. B.R. (technical product) 165–230° C. It is a solvent for cellulose nitrate and is used chiefly as a "wetting out" solution in the thread industry.

No animal experiments on this substance appear to have been carried out. Only one suspected case of injury from exposure has been reported, a case of hæmaturia reported to the Home Office in 1934, but since butyl cellosolve had also been used the association with butyl carbitol is not definitely proved.

Propylene Glycol (1·2 *and* 1·3, Dimethyl Glycol)

A colourless, odourless liquid miscible with water and alcohol.

The 1·2 variety has a B.P. of 188–9°, the 1·3 variety 214°. Propylene glycol has not been used as an industrial solvent, but is suggested as a solvent for pharmaceutical purposes. It is also used, especially in America, as an aerosol. Its low toxicity, as compared with other members of the glycol group, has been confirmed by many animal experiments. Neither by oral introduction, subcutaneous administration nor inhalation has it produced ill effects, except in very large doses.

Replacement by it of a proportion of the diet of rats even produced an increase in weight, suggesting that it could be utilised as a source of energy, and it was not until it represented 48·5 per cent. of the calorie content of the diet that fatal intoxication occurred, with post-mortem appearances of kidney and liver injury.

Subcutaneous injection of 1 c.c. per kg. 5 times a day in rabbits caused albuminuria, and the lethal dose by subcutaneous injection for mice was 5 gm. per kg. body weight (Lehmann and Flury, 1943).

Its low toxicity appears to be due to the ease with which a large proportion of it is converted in the body to lactic acid.

Propylene Glycol Monoethyl Ether

A colourless liquid miscible with water; B.P. 129–36° C. Volatility about 56 times less than that of ether. It is a solvent for cellulose esters and is used to some extent in the lacquer industry.

Toxicity to Animals

This substance appears to be slightly irritating to the eyes and respiratory organs, but inhalation of 10–30 mg./l. for 1 hour was

well tolerated, and 5 mg./l. inhaled for 8 hours daily produced only moderate kidney injury.

No cases of toxicity in human beings has been reported.

Butylene Glycol

A colourless liquid of sweetish odour, miscible with water and alcohol, insoluble in oils. B.P. 185–95° C. It is used as an intermediate in the synthetic rubber process, as a lubricant for special purposes, and has been suggested as a substitute for glycerine in the cosmetic, paper and textile industries. It is not used as a lacquer solvent.

Toxicity to Animals

Butylene glycol appears to have a low toxicity; in high doses it is a weak narcotic, and an agent of kidney injury. According to Lehmann and Flury (1943) the lethal dose by ingestion for rabbits is 15 gm. per kg. The kidney lesions consisted only of œdema and congestion.

Butylene Glycol Methyl Acetate (Butoxyl)

A colourless liquid of somewhat acid odour, miscible with water and olive oil, soluble in water to the extent of 8 c.c. in 100 c.c. water at 20° C. Volatility, 75 times less volatile than ether. It is a solvent for lacquer.

Toxicity to Animals

According to Lehmann and Flury (1943), except for moderate irritation of mucous membranes when inhaled at almost saturated vapour-air, butoxyl is practically non-toxic by ingestion, subcutaneous injection or inhalation.

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SOME ASPECTS OF MODERN ALGEBRA

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Introduction.

About a hundred years ago there was a very strong British School in Algebra. It is enough to mention that Hamilton (1805–65), Sylvester (1814–97), Boole (1815–64) and Cayley (1821–95) were active at that time and played an important part in laying the foundations of modern algebra. Since then, until quite recently, interest in the subject in this country seems to have declined in favour first of applied mathematics, under the influence of Kelvin (1824–1907), Clerk Maxwell (1831–79), Stokes (1819–1903), and Rayleigh (1842–1919), then analysis (including analytical number theory), geometry and the geometry of numbers. There were, nevertheless, a few notable algebraists like Clifford (1845–79), Burnside (1852–1927) and A. Young (1873–1940). The centre of development moved to the continent at the time of Dirichlet (1805–59), Grassmann (1809–77), Kummer (1810–93), Kronecker (1823–91), Dedekind (1831–1916), Frobenius (1849–1917), Steinitz (1871–1928) and I. Schur (1876–1941). During the last few decades Emmy Noether (1882–1935) exerted a great influence on the unification of algebra which has been felt throughout the world.

The recent revival in the study of algebra in this country has been due on the one hand to a new realisation of its intrinsic interest, and on the other to various external causes. For instance, it is on record that, during the First World War, Professor G. H. Bryan (1864–1928), when on the staff of a Government Aeronautical Establishment, did his best to convince his Director that what was required was not more men and not more guns but more algebraists ! Soon afterwards the theoretical physicist was calling out for non-commutative algebras and more recently geneticists have been asking for non-associative algebras. Algebraic geometers and topologists, among other types of pure mathematicians, now find a comprehensive knowledge of algebra indispensable. The world-wide realisation of the extensive ramifications of algebra has spread to this country and has had its effect on University appointments. We now have actual or potential schools of algebra at, among other places, St. Andrew's, Edinburgh, Manchester, Cam-

bridge and Oxford, and we can look forward to a flourishing British School.

It appears appropriate at this time to recall the ground from which modern algebra has sprung and, at the same time, to indicate some of the types of result of which it is made up. It is hoped that this will be of interest not only to those working in abstract algebra who are not familiar with its concrete background, but also to those who are not yet convinced of the importance of this subject or consider it unsuitable for undergraduate courses. It is far from our purpose either to outline a syllabus for such courses or to attempt to survey the whole subject. All we do is to remark on four of the basic ideas in algebra: *fields*, *groups*, *rings*, *ideals*; we use for illustrations results from some of the topics which have interested us personally at one time or another. Among these topics we have chosen such as are suitable for expository purposes and are comparatively unfamiliar in this country.

1. Fields and Groups

Until about a hundred years ago algebra was simply the theory of equations. From this there developed first the abstract concepts of fields and groups. The interest in this aspect arose out of the desire to determine the roots of equations, and to find when these roots could be expressed in terms of the coefficients, using only the rational operations of addition and multiplication, and their inverses, including the extraction of roots. From the geometrical standpoint there were related problems of the construction of regular polygons by Euclidean methods. Problems of constructions, using only straight-edges and dividers, led to interesting developments later.

Algebraic Numbers and Number Fields.—A root of an algebraic equation of the form

$$a_0x^n + a_1x^{n-1} + \ldots + a_{n-1}x + a_n = 0 \qquad (1)$$

where the coefficients are rational numbers is called an *algebraic number*. It can be shown that corresponding to a given algebraic number there is a unique irreducible equation (of the form (1) with $a_0 = 1$) which it satisfies. (Irreducible here means that the polynomial cannot be expressed as a product of (not constant) polynomials with rational coefficients.) The other roots of this equation are called the *conjugates* of the given number. It has been found that, without actually knowing the roots of an equation, a considerable amount of interesting information about them can be obtained. In particular we can find the equation satisfied by

a given rational function (with rational coefficients) of any root. The set $R(\alpha)$ of all rational functions (with rational coefficients) of any algebraic number α is called the *field generated by that number*. The fields generated by the conjugate numbers are called the *conjugate fields*. We can immediately distinguish a special class of algebraic equations, those of which all the roots generate the same field. Such equations (and the corresponding fields) are called *normal*. For instance, any quadratic equation is normal and so is $x^4 + x^3 + x^2 + x + 1 = 0$, but $x^3 - 2 = 0$ is not normal, since the field generated by $\sqrt[3]{3}$ contains real numbers only while those generated by the other roots contain complex numbers. The results obtained in the study of normal equations lead to results in the general case, because it can be shown that corresponding to any algebraic number α there is a normal equation such that the field $R(\beta)$ generated by (any) one of its roots β contains $R(\alpha)$ as a sub-field. Moreover, if the equation for α is given the irreducible equation for β can be found and α expressed as a rational function of β, all this without the knowledge of α.

Abstract Fields.—The fields generated by algebraic numbers are only special realisations of abstract fields. By an abstract *field* we understand any set of elements for which two binary compositions "addition" and "multiplication" are defined in such a way that (1) both addition and multiplication are associative, (2) addition is commutative, (3) addition is distributive with respect to multiplication, (4) there is a "zero element" and a "unit element," (5) "subtraction" and "division" (except by "zero") are possible. The rational numbers, which can be denoted by $R(1)$, the real numbers which we denote by **R** and the complex numbers which we denote by **C** all form fields. Neither **R** nor **C** is an algebraic number field, for any such field contains only a countable set of elements, while **R** and **C** are more than countable. Fields exist which contain only a finite number of elements; these are of interest in the foundations of geometry. They are known as Galois fields. It can be shown that in them multiplication is necessarily commutative, that they must contain p^r elements where p is some prime number and r some positive integer, and further that there is only one field with p^r elements. Any infinite field must either be *modular* (*i.e.* $pa = 0$ for some prime p and all elements a) or contain a sub-field *isomorphic* with $R(1)$. That is to say a (1–1) correspondence can be set up between the rational numbers $a, b, \ldots$ and certain elements $a', b', \ldots$ of the field in such a way that to $a + b$ and $a \times b$ there corresponds $a' \oplus b'$ and $a' \otimes b'$, where $\oplus$ and $\otimes$ denote the compositions in the field.

Abstract Groups.—Another important concept is that of an abstract *group*. This is a set of elements for which one binary composition, usually called "multiplication," is defined. (Occasionally, more especially when the composition is commutative, it is convenient to think of it as "addition" and we then speak of an "*additive group*".) We require that the composition should have the following properties: (1) associativity, (2) the existence of a unit element, (3) the existence of an inverse element with respect to the unit element. A group in which the composition is commutative is called *abelian* after Abel (1802–29). A field can therefore be described as an additive abelian group in which all the non-zero elements form a multiplicative group, the two compositions being linked by the distributive laws.

The number of elements in a group is called its *order*. Groups exist which have any finite number for order and, indeed, there may be many "distinct" (*i.e.* non-isomorphic) groups with the same order. There are two groups of order 4 and two of order 6, but there is only one group of order p, p being any prime number. Groups of infinite order exist; some with countable order play an essential part in the theory of automorphic functions, while some whose order is that of the continuum are of interest in other branches of analysis, for instance in the theory of differential equations.

The theory of finite groups, although introduced in view of its applications in the theory of equations, has been developed tremendously for its own sake apart from its applications to the theory of algebraic numbers and elsewhere; many outstanding results have been obtained and many attractive problems revealed.

Representation of Groups.—Every finite group and a large class of infinite groups can be represented by an isomorphic group of finite matrices, that is we can associate with each element of the group a matrix in such a way that to the product of two elements there corresponds the matrix which is the product of the matrices representing the two elements. Although this has been long familiar, it is only quite recently that some quite old conjectures have been established; in particular, one due to Schur, which was that every finite group of order n has for its "irreducible" representation matrices whose elements all lie in the field generated by the nth roots of unity.

A special type of representation, always possible in the case of finite groups of order n, is by means of the permutations of n objects.

A recent new application of groups of permutations has been in the determination of the relations of implication between various specialisations of the Axiom of Choice.

Galois Group.—The study of groups, like that of fields, did not start off by consideration of the abstract concept. Realisations occurred in many branches of mathematics, for instance, as groups of transformations or groups of permutations. This remark leads us back to the theory of equations. It is probably true that the introduction here of group theoretical ideas, due to Galois (1811–32), was one of the most important stages in the development of mathematics. Some algebraic fields can be mapped upon themselves in a (1–1) manner in such a way that algebraic operations are preserved—these mappings are called *automorphisms*. Suppose that α_1, a root of $f(x) = 0$, generates the field and that $\alpha_2, \alpha_3, \ldots, \alpha_n$ are its conjugates. Consider any automorphism of the field. Let α_1' correspond to α_1. Then, by definition of automorphism, to any rational function $h(\alpha_1)$ of α_1 there will correspond $h(\alpha_1')$, and in particular to $f(\alpha_1)$ there corresponds $f(\alpha_1')$. Since $f(\alpha_1) = 0$ it follows that $f(\alpha_1') = 0$, that is to say α_1' is another root of $f(x) = 0$. It is now clear that in the case of a normal equation the field in question has exactly n automorphisms and it can be shown that they form a group, called the *Galois group*, of $f(x) = 0$, which arises as a group of permutations of n objects. When the field is not normal the Galois group is defined by means of the smallest normal field in which it is contained. It is still expressed as a group of permutations of n objects.

The introduction of the Galois group enables us to classify equations of the same degree according to the structure of this group. The most significant results are obtained by examining the sub-groups of the Galois group. These sub-groups are in a (1–1) correspondence with the sub-fields of the field. The fact that a particular sub-field is normal is equivalent to the normality or self-conjugacy of the corresponding sub-group. A *normal* or *self-conjugate* sub-group of a group G is a group H contained in G which is identical with all its transforms, *i.e.* the sets of elements of the form TST^{-1}, for all S in H, for all T in G. This concept is of the highest importance. In addition to the Galois group as defined above we introduce the Galois group of a normal equation whose coefficients are in an algebraic number field A, with respect to A. This is the group of those automorphisms of the *root* field which leave every element of the *coefficient* field A invariant. Among the interesting questions here is whether a given group is a Galois group with respect to a given coefficient field. This problem is not yet solved. An important contribution was made by Emmy Noether, and recently A. Scholz (1904–42) proved that every p-group, *i.e.* a group whose order is the power of the prime number p, occurs

as a Galois group. Fields whose Galois group is abelian are of particular interest. If the coefficient field is that of the rational numbers such fields are all contained in fields generated by roots of unity.

Soluble Groups.—A group G is said to be *soluble* if an "ascending chain" $G_0, G_1, \ldots, G_n = G$ of groups exists, beginning with the group G_0 consisting of a unit element only and finishing with the group G itself, each group being a normal sub-group of its successor and the order of each G_{r+1} being a prime number multiplied by that of G_r. In particular it can be shown that every p-group is soluble. A group is said to be *simple* if it possesses no proper normal sub-groups. Both these concepts are important in the theory of equations. For instance, those equations whose roots can be expressed in terms of radicals are completely characterised by the fact that their Galois group is soluble. It is well known that the general equations of degree four or less can be solved in this way. However, as the Galois group of the most general quintic is the symmetric group S_5 of all the permutations of five objects, which is not soluble (its only normal sub-group is the corresponding alternating group which is a simple group of order 60), such an equation cannot be solved in this way. Nevertheless, it may be possible to deal with a special quintic, for its Galois group may be a soluble sub-group of S_5.

Infinite Groups.—There are many purely algebraic problems concerned with infinite groups which remain open, although recently the study of *topological* groups (when we introduce some notion of distance between their elements) has attracted most attention. Among these problems some of the most difficult are those of determining when a group, possibly infinite, is actually infinite.

Some abstract groups can be defined by saying that they are generated by certain elements subject to certain relations. For instance, the group generated by a single element T subject only to $T^n = 1$ is the cyclic group of n elements of which a realisation is the multiplicative group of the nth roots of unity. Again the group generated by S and T subject to $S^2 = T^3 = (ST)^2 = 1$ can be regarded as consisting of the six "words" 1, S, T, T^2, ST, TS. Any other word formed from the letters S and T can be reduced to one of these in virtue of the given relations. This group can be realised as the group S_3 of the permutations on three objects or as the group of symmetries of an equilateral triangle. Now consider the group generated by S and T which satisfy $S^2 = T^3 = 1$. This is of infinite order, since the "modular group" of all bilinear transformations of the form $y = (ax + b)/(cx + d)$, where a, b, c, d are integers satisfying $ad - bc = 1$, can be generated by two such

elements and is manifestly of infinite order, as it contains all the transformations $y = x + n$ for $n = 0, \pm 1, \pm 2, \ldots$. The transformation $y = -1/x$ corresponds to one of the generators and $y = -(x + 1)/x$ to the other.

An outstanding problem is that of Burnside: determine whether a group having a finite number of generators and of which each element X satisfies $X^n = 1$ for a fixed value of n is of finite or infinite order. At the moment only a few special cases of this problem have been solved.

Lattices.—The theory of lattices has thrown a new light on various branches of pure mathematics, for instance on the structure of groups. A *lattice* is a set of elements provided with two binary compositions "join" and "meet" which are denoted by $\cup$ and $\cap$. Each of these compositions is *idempotent* (*i.e.* the join or meet of an element with itself is just that element), commutative and associative. The compositions are linked by "absorptive" laws

$$a \cap (a \cup b) = a \text{ and } a \cup (a \cap b) = a.$$

It is clear that this system of postulates involves join and meet symmetrically, and it follows that to each result in the theory there is a "dual" one which requires no proof further than the present remark. This situation is familiar in projective geometry. The study of projective geometries can be regarded as a study of lattices of a special type.

The set of all sub-classes of a given class can be thought of as a lattice where the join of two sub-classes is that containing all elements belonging to one or other (or both) and their meet the sub-class containing all elements belonging to both. It is easy to verify that the various postulates are satisfied. Another example is the set of all sub-groups of a group, and yet another is the set of all sub-fields of a given field. The (1–1) correspondence between sub-groups and sub-fields mentioned earlier can be expressed as one between the lattice of sub-groups and the dual lattice of the sub-fields.

An alternative approach to lattice theory is by way of the idea of "partial order." A system is *partially ordered* if there is a binary relation "$>$" between (some pairs of) its elements which is such that (1) $a > a$ for all a, (2) $a > b$ and $b > a$ imply $a = b$, and (3) $a > b$ and $b > c$ imply $a > c$ (transitivity). The idea of bounds can be introduced in such a system. A lattice is then a partially ordered system for which every pair of elements has both a *greatest lower bound* (their meet) and a *least upper bound* (their join), both elements of the system.

Ordered Fields and Positive Definite Forms; Valuations.—The theory of abstract fields, in the same way as the abstract theory of

groups, unified various aspects of the subject and made possible the solution of problems inaccessible to more concrete methods. A classical problem, enunciated by Hilbert (1862–1943) at the Paris Congress of 1900 and which appeared out of reach of the mathematics then current, was the following:

Can a positive definite form of degree $2m$, in n variables, be expressed as the sum of squares of rational functions with rational coefficients?

It was then known that the answer was in the affirmative (even if we replace rational function by form) when $n = 1, 2$ for any m, when $n = 3$ for $m = 1$ or 2 and for any n when $m = 1$ (this is the familiar case of the expression of quadratic forms as sums of squares). In all other cases, *e.g.* when $n = 3$, $m = 3$, it was known that there were forms which could not be expressed as the sums of squares of forms. The general question was answered affirmatively some twenty years later, using the concept of totally positive elements in ordered fields.

The idea of "order" does not apply directly in abstract fields, and from a certain point of view, is foreign to algebra if this is regarded as the study of invariants of isomorphisms. However, if in a field F we can distinguish a class F_+ of elements, called "positive," such that if $a \neq 0$ then* either $a \varepsilon F_+$ or $-a \varepsilon F_+$ and such that F_+ is closed under addition and multiplication, we can develop a theory of order. For instance, we say $a > b$ if $a - b \varepsilon F_+$. It is easy to show that in an ordered field a sum of squares Σa_i^2 is always non-negative and is only zero if every a_i is. The field $\mathbf{R}$ of real numbers with the ordinary definition of positive is ordered in our sense. It is easy to prove that the field $\mathbf{C}$ of complex numbers cannot be so ordered.

Different classes F_+ for a given field give rise to different orderings of it. Nevertheless, all such classes F_+ include the sub-class of F isomorphic with the class of positive rationals.

An ordering is said to be *archimedean* if for every a there is an integer $n = n(a) > a$. Otherwise it is *non-archimedean* and in this case we have, so to speak, infinite elements, both small and large.

A notion related to that of order is valuation; this is of considerable importance in algebraic geometry (resolution of singularities). A *valuation* of a field F is a non-negative function $||x||$, defined for all elements of F, vanishing if and only if $x = 0$, and satisfying

$$||xy|| = ||x||\,||y||$$
$$||x + y|| < ||x|| + ||y||$$

* ε denotes, as usual, "belongs to" or "is a member of."

It can be proved that there are essentially only two types of valuations possible for the field R(1). The first, which is archimedean, is the case when we put, for a fixed ϱ, $0 < \varrho \leq 1$,

$$\|r\| = |r|^{\varrho}$$

for the rational number r. The second, in which the triangle inequality is satisfied in the stricter form

$$\|x + y\| \leqslant \text{max.}\ (\|x\|, \|y\|)$$

is non-archimedean and gives rise to the p-adic numbers of Hensel. Corresponding to a prime number p and a fixed number θ, $0 < \theta < 1$ we define

$$\|r\| = \theta^{n}$$

where $r = pns/t$ and s, t are integers not divisible by p, n being an integer, positive, negative or zero.

It is easy to show that if -1 is a sum of squares so is every element. In fact, if $-1 = \Sigma b_i^2$ then for any a

$$a = (\tfrac{1}{2}(1 + a))^2 + \Sigma(\tfrac{1}{2}b_i(1 - a))^2$$

Let us call the minimum N such that -1 is the sum of N squares in F the *index of disorder* of F. In particular the index of disorder of **C** is one, for $-1 = i^2$ and $i \varepsilon$ **C**; that of $R(\sqrt{-2})$ is two, for $-1 = (\sqrt{-2})^2 + 1^2$, that of $R(\sqrt{-7})$ is four, for

$$-1 = (\sqrt{-7})^2 + 2^2 + 1^2 + 1^2$$

and in each case no shorter representation is possible. The question arises as to whether fields exist which have any given integer as an index of disorder, and if this is answered negatively we can enquire as to what integers are possible indices. Three cannot be an index of disorder, for if $-1 = a^2 + b^2 + c^2$, then if

$$d = (a + bc)/(a^2 + b^2), \quad e = (b - ac)/(a^2 + b^2)$$

we have $-1 = d^2 + e^2$. It can be shown that all algebraic number fields have either 1 or 2 or 4 as indices of disorder.

The concept of "reality" is not applicable to an abstract field. However, the fact that -1 is not a sum of squares in R suggests a definition of a "*formally real*" field as one in which -1 is not a sum of squares. Certain anomalies arise from this definition, *e.g.* the field generated by a complex cube root of -2 is formally real, but in spite of them the definition has turned out to be of great value.

An element of a field is said to be "*totally positive*" if it is positive in every ordering of the field (if the field cannot be ordered all elements are considered totally positive). It can be shown that all

orderings of an algebraic number field can be obtained by mapping it isomorphically on its real conjugate fields endowed with their natural order. This enables us to define a totally positive element in such a field as one whose conjugates in all real conjugate fields are positive. The concept of totally positive was introduced by Hilbert in his *Grundlagen der Geometrie* in connection with his investigation of constructions possible by means of a straight-edge and dividers. The corresponding analytical formulation is the formation of expressions by rational operations and by taking the square root of sums of squares.

The affirmative answer to Hilbert's question can be obtained from the following two facts: (1) a totally positive element in a field is a sum of squares, and (2) a positive definite function is a totally positive element in the field of all rational functions of n variables.

2. Rings and Ideals

We have just seen how certain aspects of the theories of equations and of algebraic numbers led to the introduction of the abstract concepts of fields and groups. Considerations of the arithmetic aspect of these theories suggest the introduction of rings and ideals.

Algebraic Integers; Abstract Rings.—Exactly as we distinguish the (rational) integers $0, \pm 1, \pm 2, \ldots$ among the general rational numbers we distinguish the algebraic integers in any algebraic number field. An algebraic number is called *integral* if its equation, when the leading coefficient is unity, has *all* its coefficients (rational) integers. Any algebraic number can be expressed as the quotient of two (algebraic) integers. The sum, difference and product of two integers are again integers but, in general, their quotient is not integral. A system of elements, closed under two compositions, "addition" and "multiplication," of which the first is reversible, is called a *ring*. A ring has a *zero* but not necessarily a *unit*, as is shown by the consideration of all even rational integers with their ordinary compositions. Usually we regard the "multiplication" in the ring as a commutative operation and this will be understood unless we speak explicitly of a non-commutative ring.

The study of arithmetic in algebraic number fields is of the greatest importance, for instance, because many results about rational integers can only be completely explained by considering the corresponding facts in certain algebraic number fields. For instance, there is very often no obvious reason for the exceptional rôle which the prime number 2 plays in many parts of elementary number theory. This can often be explained by the fact that

numbers of the form $1 - \zeta_n$, where ζ_n is an nth root of unity, are exceptional in certain problems of algebraic number theory; 2 is of this form. Another instance is the well-known "quadratic law of reciprocity." Although many entirely elementary proofs of this have been given, they all seem unsatisfying and artificial in some respect or other. There is, however, a proof depending on algebraic number theory which is most revealing.

Ideals.—The peculiar difficulties which were brought along by the study of algebraic integers well repaid study, and the new concepts which it was found necessary to introduce opened up fresh possibilities in the theory of abstract rings. These difficulties reside, for the most part, in the following two facts:

(1) In many algebraic number fields it is not possible to express all numbers *uniquely* as the product of "prime" numbers belonging to the field. A standard example is in $R(\sqrt{-6})$ in which 2, 3, and $\sqrt{(-6)}$ are "prime" but where we have

$$6 = 2.3. = (-\sqrt{-6})(+\sqrt{-6})$$

(2) In most algebraic number fields there is an infinity of *unities*, *i.e.* integers whose reciprocals are also integers. For instance, in $R(\sqrt{2})$ all the numbers $\pm(1+\sqrt{2})^{\pm n}$ for $n = 0, 1, 2, \ldots$ are unities.

The first of these difficulties led to the introduction of ideals, a concept also of the highest importance in the general theory. An *ideal* in a ring is a sub-ring which contains with any element all products of that element by elements of the original ring. In the case where the ring contains a unit the multiples of a given element form an ideal, the *principal ideal* generated by that element. There are rings in which every ideal is principal; these are called *principal ideal rings.* It is not always easy to determine whether a given ideal is principal or not. Among the ideals of a ring one of the most important is its *radical.* This is the largest nilpotent ideal, *i.e.* the largest ideal for which there exists an integer n such that the product of any n of its elements is zero. The radical of **R** or **C** consists of 0 only. Some less trivial examples are mentioned below.

In the case of a non-commutative ring we can consider subrings closed under multiplication on the left, on the right or on either side and so define *left-*, *right-* or *two-sided-ideals.* The introduction of one-sided ideals is essential if we wish to obtain, for general rings, adequate generalisations of some of the results of algebraic number theory, in particular those concerned with "chain conditions."

The sum of two ideals is defined as the smallest ideal containing

both; their product is the greatest ideal contained in both. The set of all elements in the ring and that consisting of the zero element alone form ideals which can be regarded as the greatest and least elements in the lattice formed by all the ideals.

A new method in algebraic number theory has been found recently. It depends on an application of matrix theory to develop ideal theory. This is an instance of the way in which matrix theory, one of the oldest tools in modern algebra, again and again finds new applications and sheds fresh light on current problems.

Applications of Group Theory. Class Field Theory.—Group theory again plays an important part in the ideal theory of algebraic number fields. The Galois group and certain of its sub-groups, called the Hilbert sub-groups, play a large part in determining how the rational prime numbers, or rather the corresponding principal ideals, can be expressed as products of the so-called prime ideals in normal fields. One of the most important results, the Principal Ideal Theorem, has so far only been proved by means of the theory of finite non-abelian groups. The real significance of the introduction of non-abelian ideas into a theory which appears entirely commutative has not yet been discovered. This theorem for long remained a conjecture; it was first shown by Artin that it was a consequence of a certain proposition in group theory, of a type rather different from those then available. At last, after special tools were devised (which, incidentally, have greatly enriched abstract group theory) several ways to establish the proposition have been found; the first proof was given in 1929 by Furtwängler (1865–1940). It appears that there is as yet no direct proof of the Principal Ideal Theorem itself.

The Principal Ideal Theorem is one of the outstanding facts of Class Field Theory, the most important branch of modern algebraic number theory. It deals with algebraic number fields which have an abelian Galois group with respect to one of their sub-fields. These fields have been mentioned earlier. Interest in Class Field Theory was initiated by Hilbert, who not only made substantial contributions but also set up a list of conjectures—one of them the Principal Ideal Theorem—which kept mathematicians busy for a long time. Recent work on the axioms satisfied by valuations has revealed a completely new approach to Class Field Theory and may influence the whole of algebraic number theory.

Hypercomplex Systems.—An important special class of rings (possibly not commutative) are those known as *hypercomplex systems* or as *algebras*. They have a finite base with respect to a field, *i.e.* each element can be expressed uniquely as a linear

combination, with coefficients from the field, of a finite number of fixed elements. Any algebraic number field can be regarded as a hypercomplex system with R(1) as the coefficient field. The most familiar systems are those which have as coefficient field not R(1) but **R**, the field of all real numbers. In this case a system with n base-elements can be regarded as a set of vectors in an n-dimensional space with a multiplication law determined by that for the base, addition being defined by the addition of components. As special cases we mention (1) **R** itself, when there is one base element; (2) **C** when we have two base elements 1, i with $i^2 = -1$; (3) **D**, the dual numbers, which again have two base elements 1, ε with $\varepsilon^2 = 0$; (4) **Q**, the quaternions which have four base elements. In all these cases we have associative multiplication; the best-known example of a non-associative algebra is that of the Cayley numbers, which have 8 base elements.

Representations.—Hypercomplex systems which are associative can be represented isomorphically by rings of matrices. This fact, in the case of complex numbers, is used to introduce them in one of the standard text-books on complex variable theory. To $x + iy$ there corresponds the matrix $\begin{pmatrix} x & y \\ -y & x \end{pmatrix}$. The hypercomplex system, which has n^2 base elements, denoted by e_{ij}, where i, j each run from 1 to n, and where $e_{ij}e_{kl}$ is defined to be zero if $j \neq k$ and to be e_{il} when $j = k$, can clearly be represented by associating with each base element e_{ij} the $n \times n$ matrix which has all its elements zeros except that in the ith column and jth row which is 1. This system is called the *total matrix algebra of order n.*

The representation by matrices of a group-ring provides a link between those for groups and those for hypercomplex systems. A *group-ring* is a hypercomplex system whose base consists of the elements of a group with the product of elements defined accordingly.

Operators.—In order to show the significance of group-rings we select an example from Galois theory. This example involves the idea of "operators," a concept of first-rate importance especially in the connection of "groups with operator." An *operator O for a group G* associates with an element a of G another element of G which can be denoted as O(a) or a^{O} or Oa in such a way that we have, if G is a multiplicative group,

$$O(ab) = O(a)O(b) \text{ or } (ab)^{O} = a^{O}b^{O},$$

or, in the case of an additive group,

$$O(a + b) = Oa + Ob.$$

Consider a group G and a class Ω of operators O. Let g be

a sub-group of G. If $O(a) \epsilon g$ for all $a \epsilon g$ and for all $O \epsilon \Omega$ we say that g is an *allowable sub-group* with respect to Ω. For instance, if we take G as the additive group of a ring it is clear that all the elements of the ring can be regarded as operators for G if we consider them as multipliers. In this case the allowable sub-groups turn out to be the ideals of the ring. Another example is the case of a group having for operators its *inner automorphisms*, *i.e.* with any $a \epsilon G$ we associate an operator O_a, which itself associates with an element $b \epsilon G$ the element $O_a(b) = aba^{-1}$. In this case the allowable sub-groups are the normal or self-conjugate ones introduced earlier. We can also regard the additive group of a hypercomplex system as one having all the elements of the coefficient field as operators. Two isomorphic groups, which have the same class Ω of operators O and are such that if a' corresponds to a then $O(a')$ corresponds to $O(a)$ for all $O \epsilon \Omega$, are called *operator-isomorphic*.

With these definitions we can now formulate the theorem referred to above: a normal algebraic number field, interpreted as a hypercomplex system, is operator-isomorphic with the group-ring of its Galois group.

Zero-divisors.—If a hypercomplex system is a field it contains no *zero-divisors*, *i.e.* elements a, b neither of which is zero but for which either $ab = 0$ or $ba = 0$. Conversely a hypercomplex system (but not a general ring) without zero-divisors is a field. Among the systems having **R** as coefficient field and having no zero-divisors the only one which is commutative, apart from **R** itself, is the field **C** of complex numbers; the only other one which is associative is the field **Q** of quaternions. This is the famous theorem of Frobenius. The Cayley numbers form a non-associative system without zero-divisors; it is not known whether there are any other such systems, but if there are the number of elements in their bases must be a power of 2.

Structure Theorems.—The structure of hypercomplex systems has been thoroughly investigated. The classical result here is due to Wedderburn: a hypercomplex system H, modulo its radical $\mathcal{R}$, is the "direct sum" of total matrix algebras. To explain this we divide H into disjoint classes by putting two of its elements in the same or different classes according to whether their difference belongs or does not belong to $\mathcal{R}$; these classes can be regarded as a ring, the residue class ring of H mod $\mathcal{R}$, which is denoted by $H/\mathcal{R}$. As an example of this result consider the dual numbers **D**. The radical $\mathcal{R} = \mathcal{R}(\mathbf{D})$ consists of all the elements of the form $b\epsilon$ and the ring $\mathbf{D}/\mathcal{R}$ is isomorphic with **R**, which is the total matrix algebra of order 1.

Arithmetic in more general Rings.—We have spoken of the arithmetic theory of algebraic number fields. It is natural to enquire whether arithmetics can be developed in more general hypercomplex systems. The first requirement is suitable definitions for integral elements. Satisfactory arithmetics have been developed in algebras, for instance—following Gauss' arithmetic of complex numbers—by Hurwitz and others in the case of quaternions. Very recently there have been considerable contributions towards arithmetic of Cayley numbers.

Arithmetic in group-rings also leads to interesting developments.

Boolean Rings.—A class of rings rather different from the ones mentioned so far are the Boolean rings which are connected with the algebra of logic. In formal logic such combinations of propositions p, q as "p and q" and "p or q" are contemplated. This strongly suggests the consideration of the algebraic structure of the calculus of propositions. It is found that this is a special type of ring, called a *Boolean ring*, in which every element is idempotent (which implies that multiplication is commutative). The sum $p + q$ means "p if and only if q" and the product pq means "p or q"; $p = 0$ means "p is true" and $p = 1$ that "p is false." The calculus can also be interpreted as a lattice if we denote "p and q" by $p \cup q$ and "p or q" by $p \cap q$.

The study of abstract Boolean rings has been carried very far indeed; they have realisations in many different parts of mathematics and practical applications in the analysis of electrical relay circuits, for instance. The simplest of these is perhaps in the General Theory of Sets, where the elements are the sub-classes of some class. The application of algebra to the General Theory of Sets has been largely due to the Polish School, though there have been important contributions from America. Generalisations of abstract Boolean rings and lattices have been studied recently in which the associative law is omitted.

Conclusion.

In this exposition of some of the aspects of algebra we have drawn some of our illustrative examples from algebraic number theory. This theory is, at present, formidable both in extent and intrinsic difficulty, but it is far from being a closed subject. Abstract theories of great beauty have been devised in recent years to explain and illuminate known facts. The discovery of new facts is a very difficult process in view of the complexity of the numerical calculations involved in working out particular cases. The difficulties can be realised by a comparison between the vast amount of tables

in elementary number theory with the few available in algebraic number theory. For instance, although extensive tables of the ideals in quadratic fields have been prepared by Ince, only a very few types of fields of higher degree have been investigated. Such discoveries are, however, essential for the further progress of the theory. It is to be hoped that the new electronic digital computing machines will be able to provide new facts conveniently and that the rate of development in a flourishing subject will still further increase.

BIBLIOGRAPHICAL REMARKS

We have not considered it necessary, in an article of this character, to give references to the results we have quoted. Many of them will be found in the standard works on the subject, some of which are mentioned below.

The most up-to-date survey of the whole range of abstract algebra will be found in the Second Book of Nicolas Bourbaki *Les Éléments de Mathématique*. Of the nine chapters planned, only the first, *Les Structures Algébriques*, has appeared so far.

A new edition of the first volume of the *Enzyklopädie der math. Wissenschaften* began to appear in 1939, and of the articles which were published the following are relevant: Magnus on *Groups*, Krull on *Ideals* and Hermes and Köthe on *Lattices*. The volumes in the series *Ergebnisse der Mathematik*, by Deuring on *Algebras*, Krull on *Ideals*, MacDuffee on *Matrices* and van der Waerden on *Groups of Linear Transformations*, are most valuable to those with some knowledge of the subject. In the Yellow-back series there are the volume by Speiser on *Groups* and two by van der Waerden on *Modern Algebra*. Among other books in German are the *Collected Works* of Hilbert, Hecke on *Algebraic Numbers* and Zassenhaus on *Groups*, and, for the beginner, three by Hasse and one by Krull in the Göschen Collection.

Among the American books are monographs by Jacobson on *Rings*, G. Birkhoff on *Lattices*, Wedderburn on *Matrices*, Albert on *Structure of Algebras*, Murnaghan on *Group Representations*, Artin on *Galois Theory*, Menger on *Algebra of Analysis*, and two by Weyl on *Classical Groups* and on *Algebraic Number Theory*. There are useful books by Albert on *Modern Higher Algebra*, by Birkhoff and MacLane on *Modern Algebra*, by MacDuffee on *Abstract Algebra*, and several by Dickson, including *Algebras and their Arithmetics* and *Modern Algebraic Theories*. For the beginner there is MacDuffee on *Vectors and Matrices* and Albert's *College Algebra*.

Among the British books which are relevant are Turnbull on *Determinants, Matrices and Invariants*, Turnbull and Aitken on *Canonical Matrices*, Frazer, Duncan and Collar on *Elementary Matrices*, D. E. Littlewood on *Group Representations*. There are, in addition, three classics, Burnside on *Groups*, Dickson on *Linear Algebras*, Macaulay on *Modular Systems*.

There has appeared recently in Russia a book on *Group Theory* by Kurosch.

Among the expository articles we can recommend one by O. Ore, *L'Algèbre Abstraite* (*Actualité* 362, Hermann, Paris, 1936), and one by S. MacLane (*American Mathematical Monthly*, **46** (1939), 3–19).

RECENT ADVANCES IN SCIENCE

ASTRONOMY. By A. Hunter, Ph.D., F.R.A.S., Royal Observatory, Greenwich.

Of the known extra-galactic nebulæ about 97 or 98 per cent. are classified as regular, only 2 or 3 per cent. failing to show a recognisable structure. Amongst the regular nebulæ the main subdivisions are the elliptical nebulæ and the spirals, the latter having a collateral branch called the barred spirals. The elliptical nebulæ are themselves classified by decimal subdivision according to ellipticity, the globular E0 type merging imperceptibly via E1, E2 . . . to the most elongated E7 nebulæ, which are followed by the spirals, subdivided into *Sa*, *Sb* and *Sc*, in order of increasingly open structure. In the rather light-hearted way of the astronomical pioneer, the sequence was initially arranged so as to show the "early" types E0, E1 . . . merging into the "late" types . . . *Sb*, *Sc*; but these terms do not necessarily bear any temporal significance. Although nobody questions the convenience of this taxonomic arrangement, the direction in which the nebulæ are evolving is still a matter of dispute. (In an analogous case concerning the classification of stellar spectra, the astrophysicist still cheerfully speaks of the "early"-type stars O, B, A and the "late" types K, M, N, though nobody now believes that this nomenclature corresponds with the evolutionary history of the stars.) In what follows we shall not depart from established custom, but it will be well to bear in mind that "early" means "early in the sequence" and nothing else.

Now there is no doubt that all these nebulæ lie at distances far greater than the confines of our own Galaxy, and therefore that they are of galactic and not of stellar dimensions. That is not to say, however, that they have all been or indeed are all expected eventually to be resolved into separate stars. Hitherto there has been no hint of resolution in any of the ordinary E nebulæ; separate stars and condensations cannot be made out in the spirals until *Sa* or *Sb*, and even then only in the outer arms. Resolution progresses along the sequence towards the nuclei until late Sc spirals, if they are sufficiently close to us, can be completely resolved into separate stars, clusters, and bright and dark galactic nebulæ. It is tolerably certain that even the more distant Sc nebulæ, at present unresolved, would yield to higher resolving power. But however

close to us the E nebulæ are (and some are our near neighbours in the "local group" of galaxies), it is only in special cases that separate stars can be distinguished. Two such special cases are the systems in Sculptor and Fornax, referred to in these columns (SCIENCE PROGRESS, **34**, 306, 1939) at the time of their discovery and now classified as E*p* (elliptical, peculiar); the peculiarity being, in fact, such looseness of structure that they can be as completely resolved into stars as globular clusters, which indeed they resemble in most respects except overall dimensions. With these exceptions, however, elliptical nebulæ and the nuclei of early-type spirals have until now defied resolution even when they are members of the local cluster of nebulæ and are examined with the world's biggest telescope, the 100-inch reflector on Mount Wilson.

To what extent is this failure to distinguish separate stars due to the intrinsic constitution of the nebulæ concerned, and how much is it due to lack of sufficient resolving power in the observing equipment? An indication of the answer to this question comes from the spectra of E nebulæ.

With few exceptions these show the absorption lines typical of stellar reversing layers, so we may be sure that the light originates in a star or stars. It remains possible that an elliptical nebula is just a dust cloud illuminated by one or two giant stars themselves obscured by the cloud. But the evidence is against this view: where high-dispersion spectrograms are available, e.g. for the nebula M32 (type E2) the spectrum is practically indistinguishable from that of the Sun, *i.e.* it shows dwarf characteristics. Thus though the presence of diffuse obscuring matter is not excluded, the light probably comes from numbers of dwarf stars which, given sufficient resolving power, should become separately visible.

This encourages us to examine a little more closely what we mean by resolving power. Authors of text-books on Light rightly content themselves with discussing the conception in terms of physical optics. Some criterion is used for deciding whether two diffraction patterns can or cannot be separated—Rayleigh's, for example (first minimum of one pattern coinciding with central maximum of the other), gives a theoretical minimum angular separation for two stars just resolved as $1{\cdot}22\ \lambda/D$, where λ is the wave-length of the light used and D is the diameter of the (circular) objective. This criterion and others like it are used with fair success by double-star observers; and suitable modifications of it represent reasonably well the observations of faint detail on planetary surfaces. In the laboratory the expression is well attested by experience and leads to the well-known rule for resolving detail: use short

wave-lengths and big apertures. In microscopy this in turn has led to the ultra-violet and then the electron microscope. But in astronomy other circumstances prevail: atmospheric tremor and low resolving power of the photographic emulsion invalidate the expression by a factor of 20 or more; and though D is in practice kept large, the primary motive in doing so is rarely to increase resolving power, and λ is not indefinitely variable. But more important than this resolving power of physical optics is what might be called the photometric aspect of resolution. If the structure of an unresolved nebula is such that, with a given aperture, its brightest stars are below the threshold of the emulsion, then optical resolving power, however adequate in other circumstances, will not resolve them. The aperture must be increased not to increase resolving power, but to improve light-grasp. Furthermore, the question of contrast is vital. To the luminous background against which the brightest stars must be picked out contribute not only the innumerable unresolved dwarfs of the nebula but also the nocturnal radiation from the earth's upper atmosphere.

We must not expect, then, that attempts at resolving hitherto unresolved objects will be guided by optical considerations alone. Let us look now at what resolution means in extra-galactic objects already resolved: *Sc* nebulæ and the outer parts of *Sb* nebulæ. Here the stars separated are blue supergiants, stars of type O or B with absolute photographic magnitudes of −5 or −6. There is no question of making out the dwarfs or even the ordinary giants, except in those satellite systems of our own Galaxy, the Magellanic Clouds. This is incidentally just what we should expect from a study of our own neighbourhood. From the distance (say) of the Andromeda nebula an astronomer with a 100-inch telescope would see in the outer parts of our Galaxy stars such as Rigel or Deneb, not dwarfs such as the Sun or Procyon. Now the 100-inch telescope —and we must speak now of this instrument since no other is of big enough aperture for our purpose—can reach a limiting apparent magnitude of $m = 21$ on ordinary plates. Such a star at the distance of the Andromeda nebula, whose distance modulus* $m - M = 22{\cdot}4$, will have a luminosity of $M = -1{\cdot}4$. Blue supergiants in the spiral arms are therefore some 4 magnitudes above the plate

* From the definition of the stellar magnitude scale and from the inverse-square law of brightness it follows that the distance r of a star in parsecs is connected with the difference $m - M$ between its apparent and absolute magnitudes by the relation

$$\log r = 0{\cdot}2\,(m - M) + 1$$

The distance of an object can thus be as well specified by $m - M$ as by r.

threshold and are easily resolved. In the nuclear regions and in the satellite elliptical galaxies M32 and NGC 205, the fact that no separate stars are seen means that the brightest stars are fainter than $-1{\cdot}4$. This immediately suggests a comparison with the Sculptor and Fornax systems, which also contain no supergiants; and a contrast with our own galactic neighbourhood, when luminosities of -4 or -5 are by no means rare.

Until quite recently we had had to remain content with the knowledge that E nebulæ and S*a* and S*b* nuclei contained no supergiants—the task of resolving them was relegated to the 200-inch telescope still under construction in California. It came as a surprise, then, when Baade announced (*Astrophys. J.*, **100**, 137, 1944) that plates of the Andromeda nebula taken under exceptionally good conditions had shown sufficient signs of incipient nuclear resolution to make it worth while to pursue the matter further. The plates looked as if a gain of half a magnitude might be enough to show the brightest stars, but the limit imposed by sky fog on ordinary emulsions was already reached. It was possible, however, that at the sacrifice of some optical resolving power an improvement could be attained in the visual region, *i.e.* on panchromatic plates behind a yellow filter. But in this "photovisual" region the night-sky emission is particularly intense—the brightest lines in its spectrum are the forbidden OI lines at 5577, 6300, 6364 Å.—and serious fogging would result from long exposures. The only hope was in going still further into the red, where the limiting magnitude on the 100-inch is 20, giving a luminosity limit in the Andromeda nebula of $M_r = -2{\cdot}4$. If any nuclear stars were to be resolved in this wave-length region, then, they must be as bright as or brighter than $-2{\cdot}4$ in the red, whilst being (on the previous evidence from ordinary plates) no brighter than $-1{\cdot}4$ in the photographic region. Unless the brightest stars were very red, then, with a red colour-index of at least $1{\cdot}0$, even this procedure would be fruitless. But there was some reason for optimism: in the Sculptor nebula, with which we have already had occasion to compare the nucleus of the Andromeda nebula, the brightest stars *are* red giants with colour indices of this order. A trial was thus worth while, and Baade made the attempt with a plate-filter combination limiting the wave-length acceptance to the remarkably narrow range 6300–6700 Å.

This proved successful. Plates exposed for four hours in perfect seeing and with perfect figure of the 100-inch mirror finally brought out in large numbers the brightest stars in the nucleus of the Andromeda nebula (S*b*) and in its companions M32 (E2) and NGC 205 (E5). Their absolute magnitude turns out to be $-1{\cdot}1$ (photographic)

and their red colour-index 1·3, so there was very little indeed to spare. It is significant that once resolution was attained, the brightest stars appeared on these plates in great numbers. In the systems hitherto resolved, the increase in numbers, once the brightest appear, is very slow for the first few magnitudes. Nor is this the only point of difference. Baade has, in fact, distinguished two distinct types of stellar population: type I, present in spiral arms and in our own galactic neighbourhood; and type II, characteristic of early spiral nuclei and elliptical nebulæ. Type I populations can be recognised by their content of blue supergiants and open clusters, and by the characteristic "Hertzsprung gap" in their Hertzsprung-Russell diagrams. Type II populations are well shown in globular clusters, whose brightest stars are red giants, and possess a completely different Hertzsprung-Russell diagram, with the Hertzsprung gap filled by the cluster-type variables, which are rare in type I.

Now this division of stellar populations into two types cuts at the very root of stellar dynamics, and is for this reason likely to be a much more far-reaching result of Baade's work than the technical feat of galactic resolution, spectacular though that is. As Hoyle has pointed out (*The Observatory*, **66**, 108, 1945), many of our beliefs concerning the structure of extra-galactic nebulæ must be revised if Baade's classification is physically significant. Since the physical and dynamical properties of the two populations are associated with their location in a nebula, it is clear that the basic hypothesis of stellar dynamics, in which homogeneity is assumed, must be abandoned. Hoyle is not dismayed by this prospect, for he believes that other aspects of formal stellar dynamics are equally erroneous. The absence of blue supergiants from the nuclei and from the regions between the arms of spirals is accounted for at present by supposing that the mass of a spiral nebula is concentrated into nucleus and arms, with no material between. This has led to the theory that the spiral arms are "advanced" in front of the nucleus rather than "trailed" behind it. The observations are unfortunately equivocal here, but there is a good deal of evidence to show that "trailing" is the rule, and that the classical equatorial shedding of matter as a result of rotational instability in the nucleus is thus unlikely. Furthermore, Hoyle argues, there is no compelling reason to think that the general distribution of matter in a galaxy follows the distribution of its highly luminous stars. For example, if only one part in 10^5 of the mass of the Andromeda nebula were concentrated into stars ten times as heavy as the Sun, they would account for its whole luminosity; for a well-established relation

states that stellar luminosity goes with the fourth power of the mass approximately. Moreover, luminous stars are shown by Baade's work to be absent from the spiral nuclei, where the density of matter is presumably higher than in the arms. And finally, infra-red photographs of certain spirals show that they lack, in this region of the spectrum, the typical spiral formation, *i.e.* that the dwarf stars which contribute most to the mass do not outline the arms as do the giants, which, though very prominent on ordinary photographs, do not add much to the mass.

It may be that Hoyle is right in his contention that we must abandon the idea that the whole of the mass of a nebula exists in the form of stars. If so, the results of classical stellar dynamics rest on very insecure foundations, for the dynamical effects of a large proportion of interstellar matter will be profound, and its physical and gravitational properties must have played an important, if not a dominant, part in the past evolution of the galaxies, and will continue to do so in the future. And there seems no gainsaying Hoyle's further point that the highly luminous stars we see in our own Galaxy and in the arms of spirals must exhaust their supplies of hydrogen in nuclear transformations in a time (10^7 to 10^8 years) very short compared with the age of the universe ; hence either they have recently condensed from interstellar matter, or they continually replenish their hydrogen by accretion. In either case interstellar matter must be available now or have been available recently. It looks, in fact, as if an innocent attempt to push resolution of the external galaxies one stage further than it had ever been taken before may have repercussions which will shake to their foundations our concepts of galactic structure.

But there can be no halting observation whilst the theorists readjust their ideas. The next step concerns our own Galaxy. It has long been a matter of debate whether the nucleus of the Milky Way system can be detected observationally. Linked closely with this question is the role played by light absorption in space. One of the most revolutionary shifts in astronomical opinion during the last two decades has concerned the importance, if not the reality, of interstellar absorption. As recently as 1927 one of the most widely quoted and authoritative text-books on astronomy, then newly published, devoted a section to "Arguments against the absorption of light in space." Since then hardly a year has passed without bringing more and stronger evidence that interstellar absorption in the plane of the Milky Way is a factor of major importance influencing our ideas of the structure of the Galaxy. Spectrophotometric studies have revealed the frequency of space-

reddening of the light from distant stars; whilst the evidence from star counts leaves no doubt that this selective absorption is accompanied by a general obscuration, the recognition of which has caused astronomers to halve their estimates of the extent of the Galaxy. At the same time careful study, both by densitometry and by the examination of individual stars (Bowen, *Publ. Astr. Soc. Pacific*, **58**, 339, 1946), of long-exposure plates of the nearer nebulæ has shown that these are considerably bigger than had been suspected. These two factors taken together lead to the satisfactory conclusion (satisfactory, that is, to most modern astronomers, whose reaction against anthropocentric cosmology, if somewhat illogical, is historically comprehensible) that our Galaxy is not nearly such a giant among dwarfs as was supposed even ten years ago.

But it is clear that we are very ill-placed for studying our system as a whole: we cannot, as it were, see the wood for the trees. It is still not certain whether we are in a spiral nebula at all, let alone whether (if so) it is to be classed as S*a*, S*b*, or Sc. Most of the available evidence, however, suggests that it is an intermediate- or a late-type spiral. Now the nuclei of Sc nebulæ are no bigger than big globular clusters, and an object of this size would stand little chance of detection amongst the obscuring clouds in the direction of Sagittarius, where both the dynamical evidence from galactic rotation and the less direct evidence from globular clusters place the centre of the Galaxy. If our system resembles the Andromeda nebula, however, its nucleus is a much bigger entity, and the hope of detection is less remote. Such spirals seen edge-on show a large central bulge, and even if there are dense absorbing clouds between us and the nucleus, these are not likely to be so widespread as in an Sc nebula, nor, even if they were, could they be so effective in obscuring the nucleus. The question arises whether the dense, bright Sagittarius star-clouds are in fact the outer regions of the central nucleus of our system or whether they are foreground condensations behind which an obscured nucleus is beyond optical reach. The point is discussed by Baade in a paper presented to the 1946 Reno meeting of the Astronomical Society of the Pacific (*Publ. Astr. Soc. Pacific*, **58**, 249, 1946).

The nuclei of S*b* nebulæ, he points out, are made up of stars of type II. In view of the uncertainty of the coefficient of interstellar absorption it is not easy to decide the absolute magnitudes of the stars in the Sagittarius cloud, but there will be no mistaking variable stars, for which a few plates exposed consecutively serve to determine the type of variation irrespective of their distance. In an S*b* nucleus, as we have seen, these are mostly cluster-type variables,

of periods of the order of a day, whereas in local Milky Way clouds, which are presumably typical of the outer regions of the Galaxy, only 2 or 3 per cent. of the variables belong to this class. The question resolves itself, then, into deciding the predominant type of variable in the Sagittarius region suspected of being the galactic nucleus. A series of photographs of a homogeneous field at galactic longitude 328°, latitude $-4°{\cdot}3$ has been secured by Baade on the 100-inch telescope, the exposure time of 30 minutes corresponding to a limiting photographic magnitude of about 20. His preliminary examination of 10 pairs of plates on the blink comparator used for the detection of variability has resulted in the discovery of 152 variables, corresponding to a minimum density of 400 variables per square degree, which surpasses the density in previously studied Milky Way fields by a factor of 30. The crucial fact is that from 60 to 70 per cent. of the variables are of the cluster type, in striking contrast to the state of affairs in other Milky Way regions, where eclipsing variables comprise about half the total.

Already, then, it begins to look as if the Sagittarius cloud consists of a stellar population of type II. But there is further evidence of another kind that is relevant. Only the long-period variables in the cloud (these come second in the list arranged in order of decreasing frequency of occurrence) seem to surpass an apparent magnitude of 16 at maximum. The cluster-type variables are mostly encountered at about 17^m to 18^m, their numbers thence decreasing again towards the plate limit. Using a mean absolute magnitude for cluster-type variables this gives an apparent distance modulus of 17·0 or 17·5. But the reddening in this region (the globular cluster NGC 6522, which is apparently part of the cloud, has a distance modulus of 17·3 and a photoelectric colour excess E of $0^m.37$) indicates a photographic absorption (7E) of $2^m.6$, which reduces the modulus to a true (unobscured) value of 14·7. This corresponds to a distance of 9000 parsecs or 29,000 light years, in close agreement with the values obtained from many lines of evidence for the distance of the galactic centre. The Sagittarius star-cloud thus has the composition expected of the nucleus of an *Sb* nebula, and the distance expected for the galactic nucleus: confirmation both that observation by optical means in the direction of Sagittarius does in fact show us the central regions of our Galaxy, and that the Sun is a member of what is in all probability a spiral nebula of the intermediate type, like the Andromeda nebula.

PHYSICS. By F. A. Vick, O.B.E., Ph.D., F.Inst.P., The University, Manchester.

Some Problems relating to Vision.—One of the most interesting and important borderlands between the major sciences is physiological optics, demanding as it does the full resources and knowledge of physicists, physiologists, chemists and psychologists for the exploration of the wide tracts of unknown or only partially mapped territory. Two articles describing progress in parts of the field have appeared in recent numbers of this Journal. Dr. W. S. Stiles discussed the directional sensitivity of the retina (Science Progress, **33**, 676, April 1939) and Dr. W. D. Wright gave an account of the perception and measurement of colour (Science Progress, **34**, 681, Oct. 1946). These topics will thus not be treated in the present article, though mention should be made of the "Report on Defective Colour Vision in Industry," just published by the Physical Society of London, and a recent paper by Stiles "Separation of blue and green mechanisms of foveal vision by measurement of incremental thresholds" (*Proc. Roy. Soc.*, **B 133**, 418, Dec. 1946). A few of the papers published during the last year on other branches of physiological optics are summarised below.

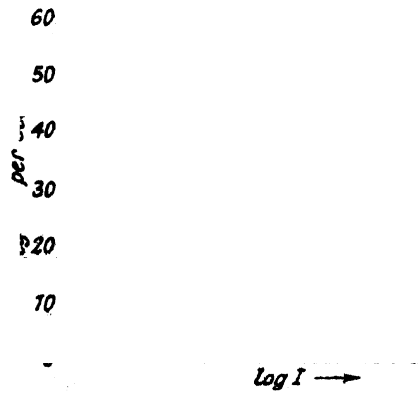


Fig. 1.

It is well known that if a white light source of given intensity is intermittent the eye perceives an unpleasant flicker unless the frequency of intermittency is above a critical value F. The critical frequency is a function of the intensity of illumination I of the retina, and a typical experimental curve of F against log I is shown in Fig. 1 (after Hecht). The curve consists of a low intensity or rod portion, and a high intensity or cone portion. If the wavelength of the stimulating light is 0·67 μ or longer, the rod section is absent, and the curve has a simple sigmoid shape. Two theories have been proposed to explain the shape of the experimental curve, (*a*) a photochemical theory due to Hecht and his colleagues, and (*b*) one based on a wide distribution of thresholds for different rods and cones so that the F – log I curves are interpreted as probability integrals

(Crozier). Neither theory is entirely satisfactory, and the question is examined by T. L. Jahn (*J. Opt. Soc. America*, **36**, 76, Feb. 1946), who proposes a reformulation of the photochemical theory. According to Hecht, a photosensitive substance S is converted reversibly into photoproducts P and A. If a is the total available concentration of S, and x the amount in the form of photoproducts, then the equilibrium equation for the pseudo-steady state at the critical frequency becomes

$$\frac{k_1 \mathrm{I}}{k_2 p} = \frac{x^2}{a - x} \qquad . \quad . \quad . \quad . \quad (1)$$

where k_1 and k_2 are velocity constants for the light and dark reactions respectively, and $1/p$ is the fraction of time during which the light is on. Hecht then, on the basis of various assumptions, derived the equation for the critical frequency F in the form

$$\mathrm{F} = \frac{1}{pk_2}(k_1 \mathrm{I})^{1/n}(\mathrm{F}_{\mathrm{max.}} - \mathrm{F})^{m/n} \qquad . \quad . \quad . \quad (2)$$

where m and n are the orders of reactions $\mathrm{S} \rightarrow \mathrm{P} + \mathrm{A}$ and $\mathrm{P} + \mathrm{A} \rightarrow \mathrm{S}$ respectively, and $\mathrm{F}_{\mathrm{max.}}$ corresponds to the maxima of the curve in Fig. 1. This equation was found to lead to various difficulties. It predicted the shift of the curve along the log I axis with change in temperature in the wrong direction, and also the wrong direction of shift with change in light-to-dark ratio. In order to fit the data on human vision it is necessary to assume the photochemical reaction to be bimolecular, which conflicts with available chemical evidence. There are other objections, which Jahn mentions in his paper, and he is led to an equation based on equation (1) but differing from (2) by adopting two main assumptions, (i) that F varies as the reciprocal of the time of the flash necessary to produce a given critical catalytic effect of freshly formed P + A just too small to cause the physiological change corresponding to a change in the sensation of brightness (the freshly formed P + A is supposed to act as a catalyst in the formation of an active agent which stimulates the nerve endings); (ii) that the maximum of F is determined not by the photochemical changes in the sense cell but by some other factor independent of temperature. The equation derived is

$$\mathrm{F} = \frac{k_4 p}{\mathrm{C}'}(\mathrm{I})^q\,(\mathrm{F}_{\mathrm{max.}} - \mathrm{F})^r \qquad . \quad . \quad . \quad (3)$$

where k_4 is a velocity constant of the catalysed reaction, C′, q and r are constants. This equation is more flexible than (2), since in the latter m and n could only be small integers (the orders of

chemical reactions), whereas q and r can have any values. Also, the temperature dependent k_4 in the numerator of (3) gives an opposite temperature shift from k_2 in the denominator of (2). Jahn shows that all known flicker data can be fitted reasonably well to his equation, which makes no assumptions regarding the photochemical cycle conflicting with the chemical evidence. It is, however, still a semi-empirical equation, and much further work is needed.

In a following paper (*J. Optical Soc. America*, **36**, 83, Feb. 1946), Jahn applies the same general photochemical theory to the dependence of brightness discrimination and visual acuity on light intensity. The photochemical cycle is

$$S \rightarrow E \rightarrow P + A \rightarrow S \qquad . \quad . \quad . \quad (4)$$

where E stands for the freshly formed catalytically active form of P + A. Denoting the concentration of E by w, the concentration of S is $a - w - x$, and application of reaction kinetics leads to

$$\frac{\Delta I}{I} = \left(\frac{C}{k_4 e}\right)^{1/q} \cdot \frac{1}{k_3 x^2 t} - \frac{1}{k_2 t} \qquad . \quad . \quad . \quad (5)$$

where $$C = k_4 e[k_1 \Delta I(a - w - x)t + w]^q \qquad . \quad . \quad (5a)$$

and e is, effectively, another constant. "t" is the time in seconds during which the light enters the eye. Equation (5) gives the ratio of the just perceptible change in illumination (ΔI) to the prevailing illumination I, and is thus a measure of the brightness discrimination. It has been shown (Hecht and Mintz, *J. Gen. Physiol.*, **22**, 593, 1939) that the critical visual angle α is proportional to $\Delta I/I$, so the same equation (5), modified only by a proportionality constant, gives the variation of visual acuity with intensity. According to Jahn, the equation can be fitted to all existing data on brightness discrimination and visual acuity, though here again much work remains before the equations can be considered to be quantitative predictions of the photochemical theory.

In a later paper (*J. Optical Soc. America*, **36**, 659, Nov. 1946), Jahn goes on to consider the kinetics of visual dark adaptation in the light of two simultaneous photochemical cycles

visual purple → transient orange → visual yellow →
visual white → visual purple
visual purple → transient orange → visual yellow →
visual purple

The general form of the curves obtained from the reaction kinetics appears to agree reasonably well with experimental data.

B. H. Crawford (*Proc. Roy. Soc.*, **B 133**, 63, Jan. 1946) has

examined the consequences of photochemical reactions in vision by measuring the course of recovery of visual sensitivity in the dark after exposure to light. For foveal vision the eye was exposed to a conditioning field of a known brightness for the requisite period (after preliminary dark adaption) and the time interval determined between cutting off the conditioning stimulus and first seeing the test field. This process was repeated for a series of intensities of the test field. For parafoveal vision, a single exposure to the conditioning stimulus was made, and then a series of threshold measurements by dropping a neutral filter over the test field as soon as seen. Analysis of the results showed that, within certain limits, the parafoveal visual process obeys the reciprocity law, *i.e.* the effects of a given "exposure" I*t* are constant, however the time *t* and intensity I are varied individually to give the same product. This means, in effect, that the reverse photochemical reaction is slow compared with the forward one in this region. In the foveal region, the reciprocity law does not hold, owing to the rapidity of the reverse reaction, except for very brief exposures. The fundamental principles of photochemistry were able to explain, in a qualitative way, the adaptation of the retina, without having to introduce any postulate involving recovery of the nervous transmission system between eye and brain.

In a recent paper, H. A. Knoll, R. Tousey and E. O. Hulbert (*J. Optical Soc. America*, **36**, 480, Aug. 1946) report the results of experiments on visual thresholds *i*, of steady point sources of light in fields of brightness *b*, ranging from zero to about 1500 candles per square foot. The data were obtained by five young experienced observers using both unaided eyes and a natural pupil. The colour temperature of the source illuminating the background and that of the point was in each case 2360° K. The point source subtended an angle at the eye of about 1 minute of arc and the background field about 12°. For the high background brightnesses, the colour temperature of the background was about 3100° K. (the change did not appear to affect the measured threshold in the overlapping range). The observers used foveal vision at high brightnesses, and extra-foveal at low. The experimental procedure was to fix the background brightness *b*, and then the observer varied the intensity of the point source several times above and below the threshold, then above the threshold and finally down to the minimum intensity at which he could just see the light all the time. Thus, "the threshold for 100 per cent. seeing" was probably a factor of 2 or more above that for which the observer saw the source for a part of the time only. The results agreed well with those recorded by

previous observers in the relevant parts of the range of b. For b less than about 3 foot candles the observed $i - b$ curve was found to be governed only by that region of the field immediately surrounding the point source out to about 0·4°, and unaffected by irregularities of brightness outside this zone, so long as no portion was brighter than b. The observations can be expressed approximately by the empirical relation

$$i = 10^{-10}(1 + b)^{1/2}. \quad . \quad . \quad . \quad (6)$$

where i is in foot candles, and b in millimicrolamberts (1 mμl. $= 2{\cdot}96 \times 10^{-7}$ candles per sq. ft.). The equation agrees with experiment within a factor of 3 over a range of b of 10^9.

A very extensive series of measurements of the contrast thresholds of the human eye is reported by H. R. Blackwell (*J. Opt. Soc. America*, **36**, 624, Nov. 1946). The entire inner surfaces of a large observation room were covered with flat white paint and illuminated as uniformly as possible over a range of brightness which could be varied between zero and 1000 footlamberts.* The end wall of the observation room served as a screen subtending 10° at the observers. The brightness of the screen was uniform to within ± 3 per cent. The brightness of the room decreased gradually towards the observer from a maximum at the screen. A standard experimental session consisted of 320 presentations of a test stimulus. The duration of the stimulus varied among experiments, but in each case a 6-second rest period followed each presentation, and additional rests at intervals prevented excessive fatigue. The observers were allowed plenty of time to adapt to the room brightness. Threshold contrast was defined as that which was detected with a probability of 50 per cent., due allowance being made for chance success (details of the statistical calculations are given in the paper). Five stimuli were used in each experiment, related approximately as 1·0 : 0·75 : 0·55 : 0·37 : 0·24 by constructing gelatine filters with appropriate light transmission which could be placed in the beam from the projector responsible for the stimulating light spot on the background screen. Each observer recorded her response by means of an 8-point selector switch connected to 8 neon lamps. The observers were women aged 19–26 with normal vision. Careful photometric measurements were made of the brightness of screen and stimulus areas. The circular stimuli varied in diameter between 121·0 and 3·60 minutes of arc. A total of approximately 220,000 observations were made for stimuli brighter than background and

* A diffusing surface has a brightness of one footlambert when it emits one lumen per square foot.

125,000 darker than background under experimental conditions differing only in adaptation brightness, stimulus area and stimulus contrast.

If B_o = background (screen) brightness,

B_s = stimulus brightness ($= B_o \pm \Delta B$)

$$\text{Contrast } C = \frac{\Delta B}{B_o}$$

Values of C range from 0 to $+\infty$ for stimuli brighter than the screen, and from 0 to $+1$ for stimuli darker than the screen. Analysis of the response data showed that there was no systematically favoured position of the stimulus spot (eight positions were used on a three-degree circle and corresponding to the eight major compass positions). A further series of experiments was carried out for longer stimulus exposures and also with the stimulus in the centre of the screen, since it was found that long exposures were necessary to obtain the minimal thresholds of contrast when the eight positions were used at random. Larger and smaller stimulus areas were also investigated. The results of the various investigations are given in the paper in tables and graphs too extensive to reproduce here, but they will undoubtedly be consulted frequently, and the method of the experiment contains many interesting features.

THE THRESHOLD OF AUDITION.—Just as the threshold value for a visual stimulus depends on the period during which the stimulus is active, and approaches a minimum value only if the period is sufficiently long, the rise of auditory threshold as the time of stimulation is reduced is readily observed. For example, if an intermittent note is on for $\frac{1}{8}$th second intervals and decreased in intensity until just inaudible, it will be heard clearly if made continuous at the same intensity. This phenomenon has been studied by J. W. Hughes (*Proc. Roy. Soc.*, **B 133**, 486, Dec. 1946). The monaural threshold was determined, starting with the shortest presentation of the note and passing progressively to the longest, finally returning to the shortest as a check. Such readings were made at frequencies of 250, 500, 1000, 2000 and 4000 cycles/sec. The mean of the two settings for the shortest duration of stimulus was taken as a reference level and the readings for the longer duration expressed as decibels below this level. When plotted in the form of (ratio of threshold intensity at any duration to that at the shortest duration) against (reciprocals of the durations), straight lines resulted, those for different frequencies being approximately parallel and displaced progressively to higher values of the intensity ratio with increasing frequency.

If I = threshold intensity for duration t secs.
I_0 = ,, ,, ,, shortest duration,
the curves are of the form

$$\frac{I}{I_0} = b + \frac{a}{t}$$

where a and b are constants at a given frequency.
If the same relation holds when $t \rightarrow \infty$ and the threshold intensity is then

$$_0\left(1 + \frac{\tau}{t}\right)$$

where τ is a constant with the dimensions of time, the results are preliminary, but they indicate that the law relating threshold and period of stimulation is of the same form in hearing as for other sensory mechanisms.

GENERAL AND PHYSICAL CHEMISTRY. By J. W. Smith, D.Sc., Ph.D., F.R.I.C., Battersea Polytechnic.

Volatile Metallic Carbonyls.—A number of investigations have been carried out during the past few years, particularly by Hieber and his collaborators, which assist in co-ordinating our knowledge of this group of compounds, a group which is of very considerable theoretical interest and also, particularly through the industrial applications of the nickel and iron compounds, of considerable practical importance. The time appears opportune, therefore, to review these compounds in general and with particular reference to the newer developments.

It may be recalled that the story of carbonyl chemistry commenced in 1890, when Ludwig Mond, with his collaborators Langer and Quincke, whilst investigating the catalytic effect of nickel on the decomposition of carbon monoxide into carbon dioxide and carbon, observed that when the nickel was allowed to cool in a current of carbon monoxide "the flame of a bunsen burner into which the escaping gas was introduced became highly luminous, and when . . . the tube through which the gas passed [was heated there was] obtained a metallic mirror which proved to be nickel mixed with a small quantity of carbon." On further investigation they concluded that the gas contained a compound of nickel with carbon monoxide which decomposed on heating at temperatures above 150° C. From the increase in volume during this decomposition they inferred that the compound was $Ni(CO)_4$. It was found that when finely divided nickel, such as is obtained by reducing

nickel oxide in hydrogen at about 400° C. is allowed to cool in a slow stream of carbon monoxide, the gas reacts very readily with the nickel, and the carbonyl, as it is now called, could be condensed out as a liquid of boiling-point 43°/751 mm., which solidified at − 25° to needle-shaped crystals. Thus was carbonyl chemistry born, and with it a great industry.

In the following year Mond and Quincke (*J. Chem. Soc.*, 1890, **57**, 604) and simultaneously Berthelot (*Compt. rend.*, 1891, **112**, 1343) observed that very finely divided iron, obtained by reducing ferric hydroxide or ferrous oxalate at only slightly above 400° and allowed to cool in hydrogen to 80°, underwent some reaction when treated with carbon monoxide, and a small proportion of the metal was converted to an analogous carbonyl. Since that time, and particularly during the past decade, a succession of other carbonyls and their derivatives have been discovered and studied.

The covalent metal carbonyls so far known are restricted to the elements of the transition groups VI*a*, VII*a*, VIII*a*, *b*, and *c*, and I*b* of the periodic table. The salt-like carbonyls of the alkali metals are quite different in character and are omitted from this review, as are the carbonyls of sulphur, selenium, and tellurium, which are analogues of carbon dioxide. The known members of the series and their simpler derivatives are summarised in Table I, where the general formulæ of the carbonyls of each group are given with, below, the metals of which each particular type has been identified.

The formulæ appear at first sight to be anomalous, since the valencies exhibited by the metal atoms seem to bear little or no relation to their normal valencies exerted in compound formation. Thus the elements of Group VI*a*, except uranium, all form hexacarbonyls, which have been shown to be monomeric. Pentacarbonyls are formed by rhenium in Group VII*a*, and by the metals of Group VIII*a*, but the latter are monomeric, whereas rhenium carbonyl is dimeric. On the other hand tetracarbonyls are formed by the elements of Groups VIII*a* and *b*, and by nickel in Group VIII*c*, these being trimeric, dimeric, and monomeric, respectively. Such tricarbonyls as are known are polymeric for Group VIII*a*, tetrameric for cobalt in Group VIII*b* and dimeric for copper in Group I*a*. These are evidently arranged in a definite pattern, but it seems anomalous that no lower carbonyl of nickel has been isolated, and that the metals of Group VIII*a* all yield the peculiar enneacarbonyls of general formula $M_2(CO)_9$. (Greek ἐννέα = nine).

At first the tendency was to regard carbonyls as ring compounds, and it was Werner who first suggested that all the carbonyl groups

TABLE I

FORMULÆ OF METALLIC CARBONYLS AND SOME SIMPLE DERIVATIVES

	Group					
	VIa	*VIIa*	*VIIIa*	*VIIIb*	*VIIIc*	*Ib*
Carbonyls	$M(CO)_6$ Cr, Mo, W	$[M(CO)_5]_2$ Re	$M(CO)_5$ Fe, Ru, Os $M_2(CO)_9$ Fe, Ru, Os $[M(CO)_4]_3$ Fe, Ru* $[M(CO)_3]_x$ Fe	$[M(CO)_4]_2$ Co, Rh, Ir $[M(CO)_3]_4$ Co, Rh*, Ir* $M_4(CO)_{11}$ Rh	$M(CO)_4$ Ni	$[M(CO)_3]_2$ Cu
Carbonyl hydrides hydrides		$M(CO)_5H$ Re?	$M(CO)_4H_2$ Fe, Ru?, Os	$M(CO)_4H$ Co, Rh?, Ir?		
Carbonyl halides halides		$M(CO)_5X$ Re	$M(CO)_5X_2$ Fe $M(CO)_4X_2$ Fe, Os $[M(CO)_4X]_2$ Os $[M(CO)_3X_2]_2$ Fe, Os* $M(CO)_2X_2$ Fe, Ru, Os $[M(CO)_2X]$ Fe, Os $M(CO)X$ Ru	$M(CO)_3X$ Ir $M(CO)_2X_2$ Rh, Ir $[M(CO)_2X_2]$ Rh $M(CO)X_2$ Co	$M(CO)_2X_2$ Pt $[M(CO)X_2]_2$ Pd*, Pt	$M(CO)X$ Cu, Au
Nitrosyls			$M(CO)_2(NO)_2$ Fe $M(NO)_4$ Fe, Ru $M(NO)_5$ Ru?	$M(CO)_3NO$ Co $M(NO)_3$ Co	$[M(NO)_2]_x$ Ni	

were directly co-ordinated to the metal atom. Still, however, the problem of anomalous valency remained until Langmuir (*Science*, 1921, **54**, 65) suggested that the carbonyls represent a class of compounds in which the metal acquires the number of electrons necessary to give it the atomic number of the next inert gas. Sidgwick called this total number of electrons, shared and unshared, which become associated with an atom its "Effective Atomic Number" (E.A.N.) (*Electronic Theory of Valency*, 1927, p. 163). If it can be assumed that each carbon monoxide molecule donates one electron pair to the metal atom, one would anticipate that, for instance, chromium, iron, and nickel, having atomic numbers which are respectively 12, 10, and 8 less than that of krypton, would take up 6, 5, and 4 molecules of carbon monoxide, respectively, and similarly for the other elements of their groups, as is observed. It was suggested by Sidgwick, and the view is now generally held, that the linkage to the metal atom occurs through the carbon atom of the carbon monoxide molecule. The Raman spectrum of nickel carbonyl shows that the frequency of the C—O linking differs only slightly from that in carbon monoxide, whilst electron diffraction measurements indicate that the four CO groups are arranged tetrahedrally about the nickel atom, with the Ni—C—O bonds linearly arranged and of lengths 1·82 and 1·15 Å., respectively (Brockway and Cross, *J. Chem. Phys.*, 1935, **3**, 825). This indicates that the six electron linkage of the carbon monoxide molecule is preserved. The zero dipole moment of nickel carbonyl, observed by Sutton, New, and Bentley (*J. Chem. Soc.*, 1933, 652) also supports this view. Similarly, chromium, molybdenum, and tungsten hexacarbonyls have the CO groups arranged octahedrally around the central metal atom (Ewens and Lister, *Trans. Faraday Soc.*, 1938, **34**, 1350).

As elements of odd atomic number cannot attain the rare gas structure by the simple co-ordination of electron pairs, they do not form monomeric carbonyls. In their highest carbonyls, rhenium, the elements of Group VIII*b*, and copper co-ordinate such a number of carbonyl groups as would be expected to give them an E.A.N. of one less than the rare gas structure, and then combine to form dimeric molecules $[Re(CO)_5]_2$, $[Co(CO)_4]_2$, $[Cu(CO)_3]_2$, etc. Further, the lower carbonyls formed by many elements are all polymeric, suggesting that the atoms which have not attained the E.A.N. of a rare gas are stabilised in some way by polymerisation.

The precise formulation of the structures of the carbonyls which contain more than one metal atom is not such a simple problem, however. To explain the case of cobalt carbonyl Sidgwick and Bailey (*Proc. Roy. Soc.*, 1934, **A 144**, 521) suggested that one carbon

monoxide molecule forms a second co-ordinate link through the oxygen atom as donor, leading to the structure

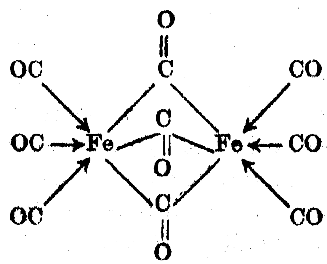
$$(O \equiv C \rightarrow)_4Co \leftarrow O{=}C \rightarrow Co(\leftarrow O \equiv C)_3$$

in which one cobalt atom has an E.A.N. of 37, and the other of 35, the excess electron on the former being passed to the latter to give each the krypton structure. A similar formulation was suggested for $[Co(CO)_3]_4$, in which the cobalt atoms were arranged at the corners of a tetrahedron and each atom was linked to each other one through a carbonyl group. This gave two cobalt atoms with E.A.N. 35 and two with E.A.N. 37, passage of electrons being again supposed to occur, so as to give each an E.A.N. of 36.

The peculiar enneacarbonyl of iron, $Fe_2(CO)_9$, was formulated by Sidgwick and Bailey as having the structure

$$(OC \rightarrow)_4Fe \leftarrow C{\equiv}O \rightarrow Fe(\leftarrow CO)_4,$$

giving each iron atom an E.A.N. of 36. Investigation of the crystal structure by Powell and Ewens (*J. Chem. Soc.*, 1939, 286), on the other hand, indicated that the iron atoms are actually 6-covalent, having three co-ordinate links from donor CO groups and three covalencies with the carbon atoms of ketonic type CO groups, so that they are formally in the ferric state. The octahedral valency angles are distorted somewhat, and the iron atoms approach close together (inter-atomic distance 2·46 Å. or about twice the covalent radius), but it is inferred that no direct linkage is formed, so that the E.A.N. of each atom is only 35. The diamagnetic character of the molecule is ascribed to the fact that the iron atoms are so close together that the electron spins are paired, although no bond is formed. The structure is thus



This observation is extremely important in view of the doubt which it throws on Sidgwick and Bailey's formulation of the cobalt carbonyls.

In relation to the structure of the carbonyls it is of interest to note that the CO groups can be replaced by one molecule of ammonia, pyridine, or alcohol, and two CO groups can be replaced by one

chelate group like ethylene diamine (en), or *o*-phenanthroline (phen) yielding $Fe(CO)_3(NH_3)_2$, $Cr(CO)_3py_3$, $Fe_2(CO)_5en_3$, $Ni(CO)_2phen$, etc.

CO groups may also be replaced by hydrogen or halogen atoms, one CO group being normally replaced by two hydrogen or two halogen (X) atoms, yielding the important series of carbonyl hydrides and carbonyl halides, *e.g.* $Fe(CO)_4H_2$ and $Fe(CO)_4X_2$. In these compounds the univalent atom seems to form a normal co-valent linkage with the metal atom, so that even atoms of odd atomic number can attain the E.A.N. of a rare gas. Cobalt carbonyl hydride, therefore, has the formula $Co(CO)_4H$ and is monomeric. Electron diffraction studies on the vapours (Ewens and Lister, *Trans. Faraday Soc.*, 1939, **35**, 681) indicate that the CO groups of both $Fe(CO)_4H_2$ and $Co(CO)_4H$ are arranged tetrahedrally around the metal atoms, and the inference is that the hydrogen atoms are linked to the oxygen atoms, so that they should be formulated $Fe(CO)_2(COH)_2$ and $Co(CO)_3(COH)$, respectively. There is also a group of derivatives of iron and cobalt carbonyls containing metal atoms, which can be regarded as salts of the carbonyl hydrides, *e.g.* $Fe(CO)_4Hg$, $Fe(CO)_4Na_2$, $[Co(CO)_4]_2Zn$, etc., since many of them with dilute mineral acids generate the carbonyl hydride.

The original, and theoretically speaking the simplest, mode of formation of the carbonyls is by the direct interaction of the metal with carbon monoxide. In the particular case of nickel the action of carbon monoxide at ordinary pressure on the finely divided metal affords good yields of the carbonyl, but with other metals use has to be made of the fact that the reaction is accompanied by a considerable decrease in volume, and is consequently favoured by an increase of pressure. Such interaction of carbon monoxide under high pressure on the metal can be used for the production of $Fe(CO)_5$, $Ru(CO)_5$, $[Co(CO)_4]_2$, and $Mo(CO)_6$. The technique for this purpose has been improved greatly by Hieber and his co-workers (*Z. anorgan Chem.*, 1939, **240**, 261). They used a rotating autoclave capable of withstanding pressures up to 350 atm. The parts which come into contact with carbon monoxide at high pressure must obviously contain no metal which is readily converted into the carbonyl, and therefore copper-silver alloys were found to be the most suitable materials for lining the autoclave. Copper itself could be used for temperatures not exceeding 200°, but at higher temperatures the components tend to become welded together.

The readiness of reaction in each case increases with the increased state of division of the metal, optimum results being obtained with metal which has been obtained by reduction of one of its compounds at the lowest possible temperature. The obvious development of

this process, therefore, is that of effecting the reduction *in situ*, utilising the carbon monoxide as reducing agent. This method was found to be particularly effective in the cases of rhenium and osmium, which yield carbonyls when their oxides are heated with carbon monoxide under high pressure, whereas no success had been obtained by using the massive metal.

The application of similar technique to the production of carbonyls from metallic halides, however, has led to a success that can hardly have been anticipated. It was found by Schulten (*ibid.*, 1939, **243**, 145) that $[Co(CO)_4]_2$, which had been difficult to obtain in good yield, could be produced conveniently from anhydrous cobalt halides in Hieber's autoclave. During the reaction no carbon oxyhalide was formed, so reaction did not seem to occur through reduction of the halide to the metal by the carbon monoxide. On the other hand cobalt iodide was shown to react with carbon monoxide even at room temperature, giving an addition compound CoI_2,CO, which is appreciably volatile, further reaction to form $[Co(CO)_4]_2$ occurring through the medium of its vapour at the copper or silver walls of the vessel. The presence of copper or silver to act as a halogen acceptor is essential to the process, and it has been found that the admixture of the finely divided metals with the cobalt halide increases the yield continuously. The yield has in general been found to be much greater from the iodides than from the bromides or chlorides, and this process, involving the intermediate formation of a carbonyl halide accounts for the previously observed fact that iodine catalyses the direct synthesis of carbonyls from carbon monoxide and the metal. This method has been used subsequently in the preparation of rhodium and iridium carbonyls, but in the case of the latter metal actual admixture of the halogen absorbing metal to the iridium halide is avoided, since this would lead to reduction directly to metallic iridium, which would not react with carbon monoxide. Instead, formation of the volatile carbonyl is permitted to occur, this coming into contact with copper or silver by diffusion.

Some other metals such as rhenium, however, appear to yield only carbonyl halides under these conditions. In this case greater success has been obtained by utilising the sulphide instead of a halide, $[Re(CO)_5]_2$ being obtainable from Re_2S_7 and carbon monoxide at 240° and 250 atm. (Hieber and Fuchs, *ibid.*, 1941, **248**, 256). The treatment of the sulphide with carbon monoxide in the presence of copper has also proved to be the best method for the preparation of $[Co(CO)_4]_2$.

Mention must also be made of the interesting series of " wet "

reactions which have been found to give rise to metal carbonyls. It has been found that alkaline suspensions of cobalt and nickel salts absorb carbon monoxide in the presence of cysteine, a sulphide, cyanide, tartrate, or amino-acid, yielding products which on acidification give $Ni(CO)_4$ and $Co(CO)_4H$, respectively. This has been developed by Blanchard and Gilmont (*J. Amer. Chem. Soc.*, 1940, **62**, 1192) as a means of producing $Co(CO)_4$. They find that carbon monoxide is absorbed quantitatively by an alkaline suspension of a cobalt salt in the presence of cysteine or cyanide according to the equation

$$2CoCl_2 + 11CO + 12KOH = 3K_2CO_3 + 2KCo(CO)_4 + 4KCl + 6H_2O$$

Addition of phosphoric acid and distillation at low pressure causes the liberation of $Co(CO)_4H$, which decomposes spontaneously at room temperature or on gentle warming giving $[Co(CO)_4]_2$.

Perhaps the most novel method of preparing carbonyls, however, is still that discovered by Job and his co-workers (*Compt. rend.* 1923 to 1928), who passed carbon monoxide into ether solutions of Grignard reagents to which metal salts had been added, and obtained small yields of the metal carbonyl. The product by this method is very pure, and it has so far proved the only successful means of preparing $Cr(CO)_6$.

Probably the largest range of carbonyl derivatives is furnished by iron and the other metals of Group VIII*a*, and it is therefore of

TABLE II

PHYSICAL PROPERTIES OF SOME METALLIC CARBONYLS

	Appearance.	m.p.	b.p.
$Fe(CO)_5$	Yellow liquid	− 20°	103°
$Fe_2(CO)_9$	Orange-yellow crystals	dec. 100°	
$[Fe(CO)_4]_3$	Green crystals	dec. 140°	
$Ru(CO)_5$	Colourless liquid	− 22°	
$Ru_2(CO)_9$	Orange crystals	sublimes	
$[Ru(CO)_4]_3$	Green solid		
$Os(CO)_5$	Colourless liquid	− 15°	
$Os_2(CO)_9$	Yellow crystals		
$[Co(CO)_4]_2$	Orange crystals	51°	
$[Co(CO)_3]_4$	Black crystals	dec. 60°	
$[Rh(CO)_4]_2$	Orange-yellow crystals	76°	
$[Ir(CO)_4]_2$	Greenish-yellow crystals	sublimes 160°	
$[Ir(CO)_3]_x$	Canary yellow cubes		
$Ni(CO)_4$	Colourless liquid	− 23°	43°
$[Cu(CO)_3]_2$	White solid	sublimes	
$Cr(CO)_6$	Crystalline solid	sublimes	
$Mo(CO)_6$	Colourless crystals	sublimes	
$W(CO)_6$	Colourless crystals	sublimes	
$[Re(CO)_5]_2$	Colourless crystals		
$Fe(CO)_4H_2$	Yellow liquid	− 70°	
$Co(CO)_4H$	Light yellow liquid	− 33°	− 26·2°
$Rh(CO)_4H$		− 12°	

interest to consider these first and in a comparative manner. $Fe(CO)_5$ is produced industrially by reducing ferric oxide with hydrogen at 500° and then passing a stream of carbon monoxide at high pressure over the finely divided metal so produced at 180–200°. The use of a flowing stream of gas is essential, as otherwise the carbonyl collects on the surface and stops the reaction. The resulting gas may contain up to 2 per cent. of the carbonyl which can be condensed out. In near ultra-violet light $Fe(CO)_5$ is dissociated forming the solid $Fe_2(CO)_9$. This compound is again unstable and when heated, *e.g.* in toluene at 95°, it undergoes disproportionation, forming $Fe(CO)_5$ and the trimeric tetracarbonyl $[Fe(CO)_4]_3$.

It was observed by Hock and Stuhlman (*Ber.*, 1928, **61**, 2097; 1929, **62**, 431) that on interaction with aqueous solutions of mercuric salts $Fe(CO)_5$ gave a dark yellow precipitate of $Fe(CO)_4Hg$, which was soluble in water, acids, acetone, ether, or pyridine, and with excess of the mercuric salt yielded the compounds $Fe(CO)_4Hg$, $HgCl_2$ and $Fe(CO)_4Hg,HgSO_4$. The compositions of these compounds were rather puzzling until Hieber and his collaborators showed that $Fe(CO)_5$ on treatment with an aqueous solution of a base, preferably barium hydroxide, underwent decomposition with the formation of metallic derivatives, which on acidification and cautious distillation at low temperature yielded iron carbonyl hydride $Fe(CO)_4H_2$ as a gas which could be condensed in a liquid air trap. Therefore the metal compounds can be regarded as derivatives of this hydride:

$$Fe(CO)_5 + 2Ba(OH)_2 \longrightarrow Fe(CO)_4Ba + BaCO_3 + 2H_2O$$
$$Fe(CO)_4Ba + H_2SO_4 \longrightarrow BaSO_4 + Fe(CO)_4H_2$$

At $-70°$ it melts to a yellow liquid which is extremely unstable excepting at temperatures below $-10°$, its decomposition leading to the liberation of hydrogen and formation of $Fe(CO)_5$, together with an ill-defined polymeric tricarbonyl $[Fe(CO)_3]_x$ of unknown complexity. It is also very air-sensitive, but owing to its acidic nature it is stable in alkaline solutions. It does not react with hydrochloric or hydriodic acids, but with iodine it gives the carbonyl iodide $Fe(CO)_4I_2$. It reduces methylene blue quantitatively, and this can be used to determine the active hydrogen present. $Fe(CO)_4H_2$ forms salts not only with alkalis but also with organic bases such as pyridine (py) or *o*-phenanthroline (phen) yielding, *e.g.* $Fe(CO)_4H_2py_2$ and $Fe(CO)_4H_2phen$, the hydrogen in this latter compound being no longer sufficiently active to reduce methylene blue.

All attempts to prepare $Fe(CO)_4H_2$ or its metallic derivatives by high pressure synthesis have failed, however, (Hieber and Teller, *Z.*

anorg. Chem., 1942, **249**, 58) although the corresponding compounds of some other metals have been made in this way.

At low temperatures $Fe(CO)_5$ adds on free halogens to give the peculiar unstable compounds $Fe(CO)_5X_2$, which all decompose below 0° giving the more stable tetracarbonyl dihalides $Fe(CO)_4X_2$. Of these the iodide was also obtained by the action of iodine on the salts of the carbonyl hydride and by the action of carbon monoxide on anhydrous ferrous iodide at high pressures. In the latter process at 18–20° the yield increases linearly with log p_{CO} and at 120 atmospheres pressure equilibrium is reached in 15 hours with 80 per cent. yield of $Fe(CO)_4I_2$ (Hieber and Lagally, *ibid.*, 1940, **245**, 305). By the interaction of $Fe(CO)_5$ with iodine monochloride and monobromide the mixed halides $Fe(CO)_4ICl$ and $Fe(CO)_4IBr$ have also been obtained. They decompose readily into two simple carbonyl halides (Hieber and Wirchling, *ibid.*, 35). Interaction of $Fe(CO)_4I_2$ or $Fe(CO)_4Br_2$ with thionyl chloride gives $Fe(CO)_2Cl_2$ as a brown crystalline solid:

$$Fe(CO)_4I_2 + 2SOCl_2 \longrightarrow Fe(CO)_2Cl_2 + I_2 + 2CO + SO_2 + SCl_2$$

It has also been shown that $Fe(CO)_4I_2$ is decomposed when heated at 200–400° in hydrogen giving $Fe(CO)_2I_2$, together with carbon monoxide and ferrous iodide, whilst on heating in carbon dioxide or nitrogen the products include the very unstable compounds $Fe(CO)_2I$ and FeI, the compositions of which have been the subject of some speculation. $Fe(CO)_2I_2$ has also been obtained by heating $Fe(CO)_4I_2$ alone or in benzene or cyclohexane solution at 80°. Carbonyl halides such as $[Fe(CO)_3Br_2]_3$ derived from the tetracarbonyl are also known.

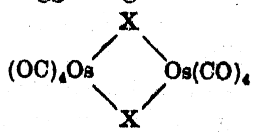
The behaviour of $Fe(CO)_5$ with bases is closely similar. At ordinary temperature it adds on ammonia or ethylene diamine yielding $Fe(CO)_5NH_3$ and $[Fe(CO)_5]_2en$, but with pyridine at 80° it yields a compound $Fe_2(CO)_4py_3$ which is pyrophoric. In the presence of pyridine other amines react with $Fe(CO)_5$ but in this case the CO groups are generally replaced by the equivalent number of other co-ordinating groups, yielding products such as $Fe(CO)_3(NH_3)_2$ and $Fe_2(CO)_5en_2$. $[Fe(CO)_4]_3$ reacts more easily with bases than does $Fe(CO)_5$, yielding the pentacarbonyl and products such as $Fe(CO)_3py$ and $Fe(CO)_3CH_3OH$. Iron carbonyl halides also react with amines, giving products which are more stable than the carbonyl halides themselves, *e.g.* $Fe(CO)_2py_2X_2$ and $Fe(CO)_2phenX_2$.

The behaviour of iron is followed closely by that of ruthenium. $Ru(CO)_5$ was first obtained by Manchot and Manchot by direct synthesis, but the best method for its production is by interaction of carbon monoxide with ruthenium triiodide in the presence of

silver at 170° and 450 atmospheres. Like $Fe(CO)_5$, $Ru(CO)_5$ undergoes photochemical decomposition yielding $Ru_2(CO)_9$, which, unlike the iron compound, is also produced spontaneously from the pentacarbonyl above its melting-point. At the same time a green solid amorphous tetracarbonyl $[Ru(CO)_4]_x$ is also obtained.

$Ru(CO)_5$ also dissolves in potassium hydroxide solution to yield a strongly reducing solution, which presumably contains the potassium salt of $Ru(CO)_4H_2$, but the latter has not yet been isolated. The interaction of ruthenium halides with carbon monoxide at lower pressures yields a series of carbonyl halides of the form $Ru(CO)_2X_2$.

The carbonyls of osmium, the highest member of the iron group, have been prepared by Hieber and Stallmann (*Ber.*, 1942, **75**, 1472 ; *Z. Elektrochem.*, 1943, **49**, 288) by the action of carbon monoxide under pressure on osmium halides in the presence of copper or silver. The best yield was obtained with the oxyiodide, prepared from OsO_4 and concentrated hydriodic acid, which at 150° and 200 atmospheres gave a mixture of carbonyls and carbonyl iodides. Another method used was to heat OsO_4 at 150–200° in carbon monoxide at over 50 atmospheres pressure. The most volatile fraction of the products contained $Os(CO)_5$ which loses carbon monoxide readily to form $Os_2(CO)_9$, which is therefore the main product of the reaction. It is noteworthy that the readiness of formation of the enneacarbonyl increases progressively with increasing atomic weight in this series. The most volatile fraction contained traces of the carbonyl hydride $Os(CO)_4H_2$, but no evidence could be obtained for the existence of $Os(CO)_4$. The other products of the interaction of carbon monoxide with the halides include not only the tetracarbonyl dihalides $Os(CO)_4X_2$ analogous to the iron compounds, but also derivatives of the types $Os(CO)_3X_2$ and $Os(CO)_2X_2$. An iodide and a bromide of the type $[Os(CO)_4X]_2$ were also identified, the dimeric character being indicated by the molecular weight and suggesting the structure



Coming to Group VIII*b*, some similarities to the behaviour of the iron group are to be observed, but there are also some sharp contrasts. The direct interaction of cobalt with carbon monoxide is an inconvenient method for the production of $[Co(CO)_4]_2$, as the metal must be in a carefully reduced finely divided state, whilst Blanchard's wet method is slow and involves tedious separations.

By far the best method is the interaction of cobalt sulphide with carbon monoxide at 200° and 200 atmospheres. The carbonyl is stable in the solid state in carbon monoxide or hydrogen, but it is readily decomposed by air or oxygen giving a violet basic carbonate. Above its melting-point it decomposes slightly to give $[Co(CO)_3]_4$.

It was found by Hieber and Schulten (*Z. anorg. Chem.*, 1937, **232**, 29) that when the tetracarbonyl was treated with baryta solution it underwent decomposition according to the equation

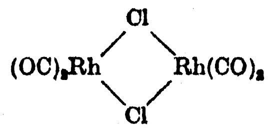
$$3[Co(CO)_4]_2 + 4Ba(OH)_2 \longrightarrow 2[Co(CO)_4]_2Ba + 2[Co(CO)_3]_3 + 2BaCO_3$$

Treatment with phosphoric acid and distillation at low pressures yielded $Co(CO)_4H$ as a light yellow liquid, b.p. − 26·2°. In contradistinction to the iron compound this carbonyl hydride is also formed in considerable yields if hydrogen or water vapour is present during the interaction of cobalt sulphide with carbon monoxide. It has also been produced by the direct interaction of $[Co(CO)_4]_2$ with hydrogen and of cobalt hydride with carbon monoxide. On gentle warming at atmospheric pressure the carbonyl hydride dissociates into $[Co(CO)_4]_2$ and hydrogen.

When cobalt or anhydrous cobalt halides are heated in carbon monoxide at high pressure in the presence of appropriate metals, "mixed carbonyls" are formed. Examples include $[Co(CO)_4]_2Zn$, $[Co(CO)_4]_2Cd$, $[Co(CO)_4]_3In$, $Co(CO)_4Tl$, $[Co(CO)_4]_3Tl$, and $[Co(CO)_4]_2Sn$. These are all typical carbonyls, being volatile solids which are non-electrolytes and are soluble in organic solvents. They are all more stable than the tetracarbonyl itself, but with aqueous mineral acids they give cobalt carbonyl hydride and the salt of the metal. No compounds of this type could be obtained, however, with lithium, beryllium, magnesium, calcium, silver, gold, germanium, antimony, or bismuth (Hieber and Teller, *ibid.*, 1942, **249**, 43). Compounds which seem to come nearer to being true salts of the carbonyl hydride are $[Co(CO)_4]_2Hg$ obtained by interaction with mercuric chloride, and the rather soluble ammines $[Co(CO)_4]_2Ni(NH_3)_6$ and $[Co(CO)_4]_2[Co(NH_3)_6]$ obtained by reaction with ammoniacal nickel and cobalt solutions. $Co(CO)_4H$ also forms a salt with *o*-phenanthroline.

It was shown by Hieber and Lagally (*ibid.*, 1943, **251**, 96) that rhodium metal on heating in carbon monoxide at 200° and 280 atmospheres yields some $[Rh(CO)_4]_2$. This behaviour may be compared with that of cobalt and contrasted with that of iridium, which does not yield carbonyls on the direct interaction of carbon monoxide with the metal. When rhodium halides are heated in carbon monoxide at 50° to 80° and 200 atmospheres, however, in the presence of copper, silver, or zinc as halogen acceptor, the product

is the tricarbonyl $[Rh(CO)_3]_x$, whereas at 80 to 230° $Rh_4(CO)_{11}$ is formed. This latter carbonyl is characterised by its comparatively high stability, being for instance unattacked by dilute acid or alkali and having a low solubility in organic solvents. Rhodium carbonyl hydride, $Rh(CO)_4H$, had been previously prepared (Hieber *et al.*, *ibid*, 1939, **240**, 261; **243**, 145, 156) by heating the metal in a mixture of carbon monoxide and hydrogen of partial pressures 200 atmospheres and 50 atmospheres, respectively (*cf.* $Co(CO)_4H$), and by the interaction of hydrated rhodium trichloride and carbon monoxide at 200° and 200 atmospheres. It melts at − 10 to − 12°, and like the cobalt compound loses hydrogen readily above its melting-point giving $[Rh(CO)_4]_2$. A series of crystalline carbonyl halides of the type $Rh(CO)_2X_2$ has been prepared by the interaction of the trihalide with carbon monoxide at ordinary or higher temperature, according to the halide used. These compounds are volatile, the molecular weight of the chlorine compound corresponding to the dimeric formula and suggesting the structure



The dry iridium trihalides $IrCl_3$, $IrBr_3$, and IrI_3 when heated in the silver- or copper-lined autoclave with carbon monoxide at 140°, 110–120°, and 90–100°, respectively and at 350 atmospheres, yield iridium tricarbonyl $[Ir(CO)_3]_x$. On the other hand, when K_2IrBr_6 is heated in carbon monoxide at 125° and 200 atmospheres, and the product sublimed in carbon monoxide, $Ir(CO)_3Br$ is formed as brown scales. This suggests that the reaction in each case proceeds via the carbonyl halide and not through the initial production of the metal. Indeed the addition of copper or silver to the iridium halide itself is avoided as it leads to reduction to metallic iridium at the temperatures used, and the metal does not react with carbon monoxide. With complex halides such as $(NH_4)_2IrCl_6$, Na_2IrCl_6 and K_2IrCl_6 the addition of the halogen-absorbing metal is necessary in order that the halogen is to be replaced completely, the product being a mixture of $[Ir(CO)_3]_x$ and $[Ir(CO)_4]_2$, separable by utilising the slight solubility of the tetracarbonyl in carbon tetrachloride or ether, or by fractional sublimation. The $[Ir(CO)_4]_2$ readily loses carbon monoxide giving the tricarbonyl, which is resistant to attack by concentrated acid, dilute alkali, or halogens at room temperature. On the other hand, with chlorine at 200° it yields crystals of $Ir_3(CO)_4Cl_9$. The molecular weights of these carbonyls have not been determined owing to their low solubilities, but the general

behaviour of the tetracarbonyl is in accord with the dimeric formula. The strong tendency of iridium to form carbonyl halides is shown by the fact that interaction of carbon monoxide with the appropriate halide at atmospheric pressure and 150° yields the compounds $Ir(CO)_2X_2$ and $Ir(CO)_3X$.

On the other hand, if moist $IrCl_3$ is heated in carbon monoxide at high pressures a volatile compound is produced, which on passing through a strongly heated tube deposits an iridium mirror, suggesting the presence of $Ir(CO)_4H$ (Hieber and Lagally, *ibid.*, 1940, **245**, 321).

The position in Group VIII*c* is most peculiar. $Ni(CO)_4$ is by far the most easily prepared of all carbonyls, being very readily obtained by direct synthesis. It is a liquid which is miscible with most organic solvents and is unacted upon by aqueous acids or alkalis. It reacts only slowly with oxygen alone or in the presence of water, yielding a variety of products. On the other hand there are very few derivatives formed. It is readily attacked by halogens, but so far reaction always seems to proceed to completion with the formation of the nickel halide and carbon monoxide; in fact no carbonyl halide or carbonyl hydride has been described. On treatment with pyridine or *o*-phenanthroline, however, partial replacement only of the CO groups occurs, with the formation of such compounds as $Ni_2(CO)_4py$, $Ni(CO)_2py$, $Ni_2(CO)_3py_2$, and $Ni(CO)_2phen$.

By contrast, no pure carbonyls of the other members of this group (palladium and platinum) have been described, whereas carbonyl halides such as $PdCl_2(CO)$, $PtCl_2(CO)$, $PtCl_2(CO)_2$, and $Pt_2Cl_4(CO)_3$ have long been known as formed by the interaction of the halides with carbon monoxide.

Coming to Group I*b*, Bertrand (*Compt. rend.*, 1923, **177**, 997) and Zelinski (*ibid.*, 1041) obtained copper mirrors by treating cupric oxide with carbon monoxide, and attributed this behaviour to the formation of copper carbonyl, but only recently has $[Cu(CO)_3]_2$ been isolated by Robinson and Stainthorpe (*Nature*, 1944, **153**, 24) by interaction of carbon monoxide with heated cuprous oxide. It sublimes readily and its vapour is dissociated at higher temperature with the deposition of copper. Its properties are in accord with the dimeric formula. Previously the only carbonyl derivatives of this group were the product $Cu(CO)Cl,2H_2O$ obtained when carbon monoxide is absorbed by cuprous chloride solution, a gold compound $Au(CO)Cl$, and a silver sulphate addition compound Ag_2SO_4,CO.

The carbonyls of the Group VI*a* metals molybdenum and tungsten can be obtained by direct synthesis, but $Cr(CO)_6$ has so far been produced only by Job's Grignard reagent method. Nesme-

janov and his co-workers (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **26**, 54, 58) have also obtained $Mo(CO)_6$ by reducing $MoCl_5$ at -10 to $0°$ by carbon monoxide and iron or zinc dust in ether-benzene mixtures or better in dry acetone, and $W(CO)_6$ by similar reduction of WCl_6, preferably in dry ether. The intermediate formation of a sub-halide unstable at low temperatures was tentatively suggested to explain the low yields of 10–14 per cent., which were improved by increased initial pressures of carbon monoxide. $WOCl_4$ in ether also gave $W(CO)_6$ under these conditions, but no carbonyls could be obtained from WO_3 or $CrCl_4$. These hexacarbonyls are all characterised by a remarkable stability, decomposition commencing only at about 120° with the formation of pure metallic mirrors. At ordinary temperature they are unattacked by concentrated hydrochloric or sulphuric acid, but are oxidised rapidly by concentrated nitric acid. With alkali no carbonate or carbonyl halide is formed, this behaviour being analogous to that of nickel carbonyl. No carbonyl halides have been obtained through the interaction with halogens; actually $Cr(CO)_6$ is unattacked by bromine or iodine but otherwise they yield the metal halides and carbon monoxide. The extreme stability of these carbonyls is also exemplified by the difficulty of obtaining amine derivatives, although a number of these have been isolated by Hieber and his co-workers; examples are $Cr(CO)_4py_2$, $Cr_2(CO)_7py_5$, $Cr(CO)_3py_3$, $Cr(CO)_3py$ phen, and $Mo(CO)_3py_3$, in each of which the co-ordination number of the metal atom remains at a value of 6.

Lastly, in Group VII*a* no carbonyl derivatives of manganese have been described. The second element of the series, discovery of which was claimed by Noddack, who called it masurium, has been obtained in appreciable quantities only recently as one of the products of atomic fission, so its carbonyl derivatives, if any, have not yet been investigated. A series of such compounds of rhenium are known, however. It has so far not been found possible to prepare $[Re(CO)_5]_2$ directly from the metal and carbon monoxide, but good yields have been obtained by the interaction of carbon monoxide with Re_2O_7 at 250° and 350 atmospheres, $KReO_4$ at 270° and 500 atmospheres, or Re_2S_7 at 240° and 250 atmospheres. In the presence of hydrogen or water vapour small quantities of a volatile compound, possibly the carbonyl hydride $Re(CO)_5H$ are also formed. $[Re(CO)_5]_2$ is a colourless crystalline compound, which may be sublimed and which is soluble in organic solvents, cryoscopic measurements in which confirm its dimeric structure (Hieber and Fuchs, *Z. anorg. Chem.*, 1941, **248**, 256). With amines it reacts similarly to the Group VI*a* carbonyls, generally with the replacement

of CO groups, yielding *e.g.* with pyridine at 250° $Re(CO)_3py_2$ and with *o*-phenanthroline $Re(CO)_3$phen. With halogens it gives the carbonyl halides $Re(CO)_5X$, which had also been obtained during earlier attempts to produce the carbonyl by heating the halogenorhenates K_2ReX_6 and other rhenium halogen derivatives in carbon monoxide at high pressure, and from carbon monoxide, rhenium and a dissociable nickel or copper halide or carbon monoxide, potassium perrhenate, and an organic halide (Schulten, *ibid.*, 1939, **243**, 164; Hieber, Schuh, and Fuchs, *ibid.*, 1941, **248**, 243). In the interaction of carbon monoxide with K_2ReX_6, Schulten found the ease of reacton to increase in the order $Cl < Br < I$. In fact, in the presence of copper powder $Re(CO)_5I$ is formed at 1 atmosphere and 200°, whereas 10 atmospheres and 300° are required for the bromide and higher pressures still for the chloride. These carbonyl halides are stable in air and insoluble in water, but soluble in organic solvents. They can be sublimed in carbon monoxide, the volatility decreasing from the iodide to the chloride, this also being the order of increasing stability, as the iodide is easily converted into the bromide and the latter into the chloride by the action of the appropriate halogen. Unlike other carbonyl halides all attempts to remove the halogen by the action of silver have been unsuccessful. On the other hand they react with bases giving substitution products such as $Re(CO)_3Clpy_2$ and $Re(CO)_3$Clphen.

Little contribution has been made recently, however, to the study of the nitrosyls and carbonyl nitrosyls of the metals. The present position in this direction seems to be that, generally as a result of interaction of nitric oxide with the carbonyl or carbonyl hydride, the existence of fairly stable compounds $Co(NO)(CO)_3$ and $Fe(CO)_2(NO)_2$ has been confirmed, whilst other compounds of the formulæ $Fe(NO)_4$, $Ru(NO)_4$, $Ru(NO)_5$, and $Co(NO)_3$ have been described. The two well-established compounds accord with the views of Sidgwick that the NO group not only co-ordinates to the metal atom, but also passes one electron over completely to the shell of the metal atom, thus increasing its E.A.N. by three. This aspect of the subject, however, merits further investigation

In so far as the practical applications of these compounds are concerned, the use of carbonyl formation in the Mond nickel process and of iron pentacarbonyl in the production of very pure iron are well known. The frequency with which methods for the production of other carbonyls have appeared in recent patent literature, however, suggests that other uses of this group of compounds have been envisaged. These doubtless include their uses as catalysts for various types of reactions, but the possibility of utilising the

different conditions for carbonyl formation in the separation of the platinum metals must also be considered.

BIOCHEMISTRY.

By W. O. KERMACK, D.Sc., LL.D., F.R.S., Royal College of Physicians' Laboratory, Edinburgh.

PROTEINS AND AMINO-ACIDS

OF all the known constituents of the living cell, the proteins present the most challenging problems to the investigator. They seem to be absolutely indispensable for life as we know it. Protein forms the major constituent of the simplest viruses; the common enzymes are proteins mainly, if not completely, and enzymes are the promoters and regulators of practically all the chemical reactions which go on within the living cell. From the chemical point of view, the composition of proteins is at the same time both very simple and very complex. As is well known, a protein molecule consists of some hundreds of amino-acids united to each other by peptide linkages, that is to say the carboxyl group of one acid has united with the amino group of the next to form an amide group, and in this way a chain of amino-acids is formed which is the characteristic feature of the protein molecule. For this fundamental knowledge of protein structure we are indebted mainly to Emil Fischer. During the past forty years, innumerable investigations have been made, physical, chemical, and physico-chemical, with the object of giving us a more precise knowledge of protein structure. Powerful weapons, such as X-ray analysis, have been brought to the assault, but a typical globular protein, such as insulin or crystalline egg-albumin, seems to be too complex to be readily overcome even by such powerful engines of investigation. X-ray analysis in the hands of Astbury has given us a general picture of the relatively inert fibrous proteins such as keratin and fibrinogen, and no doubt as time goes on this and other physical methods will become increasingly fruitful.

These physical methods may be expected in the first place to give us information about the general plan of the protein molecule, its form and overall pattern. It is obviously of the greatest importance that this general knowledge of structure should be supplemented by facts of another sort. Since the time of Fischer it has been one of the major tasks of the protein chemist to analyse the complete proteins in terms of the constituent amino-acids. This has proved a difficult and laborious task. There may be some two dozen or so different amino-acids in a typical protein and we are not yet quite sure that all the naturally occurring amino-acids have been identified. Some of these amino-acids closely resemble

each other in physical and chemical properties. Most of them are extremely difficult to isolate quantitatively in a pure form. The result is that, although numerous highly skilled chemists have spent many years of labour analysing proteins, it is perhaps only recently that the amino-acid composition of a few selected proteins has become known with any approach to completeness and accuracy. Important contributions have recently been made by Chibnall, and some of his results and the conclusions to be deduced from them regarding protein structure in general have been presented in a recent lecture (*Proc. Roy. Soc.*, 1942, **B 131**, 136–60).

PARTITION CHROMATOGRAPHY.—In view of the importance and the difficulty of protein analysis it is not surprising that new methods should have been searched for and exploited with energy and ingenuity. One of the most successful and remarkable of these novel methods is that developed by Martin and Synge and described in a series of papers in the *Biochemical Journal*. The methods which have been devised by these workers are very important as methods, for they are evidently capable of many fruitful applications outside the limits of protein chemistry as well as within. The results which Martin and Synge, in a few short years, have obtained by the use of these methods are already most impressive. A brief summary can scarcely do justice to the wealth of ideas contained in the original papers.

The method, which the authors have called "partition chromatography," involves three basic ideas. The first is that, in order to separate two compounds, use may be made of differences in their partition coefficients in two immiscible liquids, *e.g.* chloroform and water. When the coefficients are of quite different orders, if, for example, we have a mixture of cholesterol and sodium chloride, there is of course no difficulty in effecting the complete separation by using water and chloroform, and the method in this extreme form is as old as chemistry itself. If, however, the partition coefficients differ only slightly, very many partitions are required to effect appreciable separation. The second important element in partition chromatography is the principle of the countercurrent process. One form of countercurrent process may be conveniently represented as in Fig. 1.

E′	D′	C′	B′	A′				
				A	B	C	D	E

FIG. 1.

A, B, C, D, E, etc. represent a series of test-tubes containing each the same volume of water; A, in addition, contains two dissolved solutes, X and Y. The tubes A′, B′, C′, D′, etc. each contain

a given volume of a solvent immiscible with water, *e.g.* chloroform saturated with water. First of all the contents of A and A′ are shaken together, the chloroform and water layers separated and returned to their respective tubes. Then the chloroform tubes are moved along one stage, so that A′ corresponds with B, and B′ with A. The contents of the corresponding pairs are again shaken and again separated. The chloroform tubes are moved on one more stage; the corresponding pairs are now A′C, B′B and C′A; these are now shaken and separated. This process of moving, shaking, and separating, is continued as long as necessary.

Clearly, after one operation, X and Y are distributed between one water and one chloroform tube; after two operations between two water and two chloroform tubes, and so on. After n operations, n tubes of water and n of chloroform will be involved. It is not difficult to show that the highest concentration of X will now occur in one of the tubes, say the rth one, and that the concentrations in the other tubes will regularly decrease towards the ends of the row. As n increases, so does r, that is to say, as the series of operations is continued, the tube of maximum concentration moves regularly on. But, in addition to the maximum moving on, the compound X is distributed over an ever larger number of tubes; the "spread" increases and the maximum is less sharp.

Now the rate at which the maximum moves along depends directly on the distribution coefficient between the chloroform and water. Thus if the coefficients for X and Y differ slightly, the maximum tube for X will differ from the maximum for Y, and this difference will increase with n, the number of operations. The process of separation, however, of the two compounds is complicated by the increasing "spread" of each among the tubes. Fortunately the separation of the maxima is proportional to n, while roughly speaking the "spread" is proportional to only the square root of this number, so there is always a net advantage with increasing n.

Craig's Method of Countercurrent Distribution.—It is useful to have this simple form of countercurrent distribution in our minds when discussing the work of Martin and Synge, though these authors did not apply the idea quite in this form. We may digress for a moment, however, to refer to a series of papers by Craig who, with some success, has exploited the possibilities of this very simple set-up. Apart from emphasising and demonstrating some of the possibilities of the method, Craig (*J. Biol. Chem.*, 1944, **155**, 519) has developed an apparatus whereby the numerous shakings and separations which are involved in one step of the above process may

all be conveniently carried out simultaneously. Even with a set of eight tubes thirty-six different distributions and separations are involved and, with ordinary separating funnels, this is somewhat laborious and time-consuming; but with Craig's apparatus values of $n = 20$ or over may easily be reached, and so partial separations may be achieved with relatively little difference in the distribution coefficients. The main advantage of Craig's method of counter-current distribution is that at every operation it is precise and definite and so lends itself to quantitative control. A pure substance gives an amount of spread about the maximum tube which can be calculated theoretically, and if this "spread" is exceeded, or the distribution is unexpectedly asymmetrical, the presence of a second substance is indicated. Of course, if two compounds are present with very different distribution coefficients they become partially separated relatively quickly and their presence is easily recognised by the development of two maxima.

An interesting example of the application of the method is found in a recent paper (Elderfield, Craig *et al.*, *J. Amer. Chem. Soc.*, 1946, **68**, 1516), where it is shown by countercurrent distribution analysis that plasmoquin, as ordinarily prepared, is not—as previously thought—a pure substance, but is a mixture of two isomeric bases. It has also been used in the separation and crystallisation of pure synthetic penicillin recently reported by du Vigneaud, Carpenter and Holley (*Science*, 1946, **104**, 431).

Countercurrent Processes in General.—Martin and Synge have developed countercurrent methods in a different direction. Instead of the discontinuous process outlined above they have concentrated on continuous countercurrents. We have to imagine not the two sets of test-tubes, containing water and chloroform respectively, but a stream of chloroform moving in one direction past water moving in the other.

Perhaps it is simplest to imagine the water forming a vertical column and chloroform, emulsified into droplets, falling down through this column of water. At every point in its downward course the chloroform droplet is supposed, almost instantaneously, to reach equilibrium with the surrounding water in respect of the distribution of the dissolved solute between chloroform and water. This is the general idea of continuous countercurrent distribution; the problem is to overcome the technical difficulties that are met with in attempting to control two mobile liquid phases.

Continuous countercurrent processes have been developed more extensively for large-scale use in industry than in the laboratory. The best-known example of a countercurrent process is perhaps

fractional distillation. In the fractionating column, vapour rises upwards, and a stream of liquid descends. In the simplest type of column there is a series of perforated plates which bring about close contact, and thus equilibration of liquid and vapour, so that the liquid falling from a plate and the vapour ascending from it are in equilibrium. Each plate in fact effects a separate distillation, and the efficiency of the column in separating any particular pair of liquids simply depends on the number of plates. This type of column is essentially discontinuous in its action ; there is supposed to be no interaction between vapour and liquid in the space between the plates. In practice, however, a fractionating column very often consists of a tube filled with suitably shaped small beads or pieces of steel. The liquid trickling down and the vapour bubbling up are then mixed continuously. Such a column, it has been found, is equivalent in its efficiency to one containing a given number of plates, and so it is customary to refer to the efficiency of any column in terms of the number of plates to which it is equivalent. This "packed" type of column is analogous to the continuous counter-current distribution we are now discussing.

IMMOBILISATION OF THE AQUEOUS PHASE.—Martin and Synge (*Biochem. J.*, 1941, **35**, 91) investigated countercurrent distribution methods on a laboratory scale and developed a somewhat complicated piece of apparatus for carrying out the process automatically. It was, however, soon superseded by a much more elegant device in which use was made of a new idea, the third element in partition chromatography (Martin and Synge, *Biochem. J.*, 1941, **35**, 1358). This idea was to fix one of the two liquid phases by immobilising it in particles of a gel or some other suitable material. The gel chosen was silicic acid. This most effective device converted the whole process into a very simple one. A tube, about 1 cm. in diameter, 30 or 40 cm. long, provided with a perforated base, is set up vertically, and partly filled with suitably prepared silica gel. The material to be analysed is applied in a little chloroform to the top surface of the gel. Chloroform, saturated with water, and containing perhaps 1 per cent. of butyl alcohol, is poured into the column, and the chloroform is allowed to percolate down between the particles of the gel. The dissolved compound rapidly equilibrates itself between the water in the minute particles of the silica gel and the chloroform as it percolates downwards. Now just as the continuous fractionating column may be conveniently discussed in terms of the equivalent "plate-column," so for theoretical purposes this silica column may be considered as composed of numerous sections, in each of which the chloroform comes into complete

equilibrium with the water before passing on to the next. The width of these sections depends on the inefficiency of the continuous process due to the time taken to reach equilibrium, which does not occur instantly, and to processes such as diffusion which reduce efficiency. This theoretical division of the column into "plates" is, in fact, a device to allow for deviations from perfection and permits the theory of the discontinuous process already described to be utilised.

In practice the method has obviously a very close resemblance to the now well-known chromatogram. There is, however, one important difference. In the ordinary chromatogram the process involved is adsorption on the surface of the material of which the column is composed. Compounds are separated in virtue of differential adsorption. In the present method, the essential process is the partition of the compounds between two liquids. The silica does not play any active part, but merely provides an inert solid support for the water and prevents it from moving in the chloroform stream. For this reason the authors have given it the name of partition chromatography.

Partition chromatography was developed with the initial object of examining the amino-acids obtained on the hydrolysis of a protein. It was found that, owing to adsorption on the silica, the amino-acids themselves did not work well, but that their acetyl derivatives, obtained from them by the action of acetic anhydride, were very much more satisfactory. Each acetylamino-acid is carried by the chloroform down the silica column at a rate depending on its partition coefficient between chloroform and water. As might be expected, the band widens slightly as it progresses, but this broadening of the band is often relatively slight in proportion to the distance travelled. This means that each unit length of the column is equivalent to a large number of "plates" or separate distributions in the equivalent discrete distribution process; the authors estimate in fact that each centimetre of the column corresponds to several hundred "plates."

But the acetylamino-acids are colourless compounds; how are the various bands to be detected? The answer of Martin and Synge is characteristically simple and elegant. In the silica gel they incorporate a little indicator, *e.g.* methyl orange. The presence of the acetylamino-acid is shown by the indicator becoming reddish, and, as the chromatogram is developed by the chloroform, the various bands may be readily followed as they move downwards.

As the bands pass out of the bottom of the column, the chloroform carrying the acid may be collected and the amount of acid

determined by titration. Control experiments on mixtures of known amounts of acetylamino-acids show that recoveries of nearly 100 per cent. are often obtained, though with some acids the results are not quite so good. It is not always easy to separate all the amino-acids which may occur in a protein from each other and so certain of them are grouped together in presenting the analytical results. The power of the technique is indicated by the fact that an analysis of the amino-acids present in about 30 mg. of Merino wool gave results in substantial agreement with those obtained by previous more laborious and time-consuming methods.

Filter-Paper Partition Chromatography.—The later developments of partition chromatography are even more remarkable. It occurred to Gordon, Martin and Synge (*Biochem. J.*, 1943, **37**, Proc. xiii) to use cellulose instead of silica gel to support the water phase. Now, a common and fairly pure form of cellulose is filter-paper, so that the silica column was replaced by a strip of filter-paper. One immediate advantage of replacing silica by cellulose was that the unacetylated amino-acids could now be employed, as the difficulties previously met with, due to their adsorption on the silica, were no longer encountered. The method is fully described by Consden, Gordon and Martin (*Biochem. J.*, 1944, **38**, 224). A strip of filter-paper, a foot or two long, is suspended in a chamber which has an open vessel containing both water and the second solvent at the foot, so that the atmosphere of the chamber is kept saturated with both vapours. The filter-paper does not need to be specially wetted, but takes up 20 or 30 per cent. of water, which acts as the fixed aqueous phase. Near the top of the strip is put a drop of the solution containing the amino-acids under investigation. The second solvent, *e.g.* water-saturated phenol or collidine, is contained in a trough into which the top of the filter-paper strip dips. Under the action of capillary forces a film of this solvent works its way down the strip and it carries the amino-acids down with it, each at its own characteristic rate. The rates, of course, depend on the particular solvent employed and to some extent on the precise conditions of the experiment. After a few hours, when the advancing edge of the solvent has nearly reached the end of the strip, the paper is dried, and the presence of the colourless amino-acids is revealed by treatment with ninhydrin, with which amino-acids develop a blue colour. A series of blue spots on the filter-paper strip indicate the various amino-acids, and these can be identified by their position, for each amino-acid under given conditions travels at a definite rate. All the distances involved, of course, depend on the amount of travel of the solvent, and this is

readily measured in terms of the position of the edge of the advancing film, which is easily seen and marked on the filter-paper.

Now we come to a very fascinating development of this most flexible technique. The filter-paper strip, like the silica column, is essentially one-dimensional. Consden, Gordon and Martin (*loc. cit.*) have developed two-dimensional chromatography. Instead of a strip, they use a rectangular piece of paper. The drop containing the amino-acids is applied near one corner, and the chromatogram developed by a suitable solvent in the usual way. The amino-acids will now be distributed in spots down a line near one of the vertical edges of the paper. The paper is dried, turned through a right angle, so that the acids are now along the top of the paper, and the chromatogram again developed, this time with a different solvent. The various amino-acids are now distributed in two dimensions over the surface of the paper. The paper is dried and the positions of the amino-acids revealed in the usual way by treatment with ninhydrin. The point of the two-dimensional chromatogram is that any two acids which happened to have the same rate of travel with the one solvent are extremely unlikely to have the same rate with the other, so that effective separation of all the acids from each other is much more certain. In short, each amino-acid is now characterised not by only one co-ordinate but by two, which are usually independent of each other, and this of course much facilitates separation and identification. Using the hydrolysis product from 200 to 400 micrograms (0·2–0·4 mg.) of wool, Consden, Gordon and Martin were able to identify all the known amino-acid constituents by the help of this most powerful analytical tool.

The method of partition chromatography is still in its infancy, but already it has yielded results as interesting as is the method in itself. Gordon, Martin and Synge have applied it to the analysis not only of the amino-acids derived from proteins, but also to the identification of the partial hydrolysis products, the di- and tri-peptides. These peptides give us information about the order in which the amino-acids are arranged within the protein molecule. This may be illustrated by an example recently published (Synge, *Biochem. J.*, 1945, **39**, 363; Consden, Gordon, Martin and Synge, *ibid.*, 1946, **40**, Proc. xliii), which we shall now briefly discuss.

Structure of the Antibiotic, Gramicidin-S.—Gramicidin-S, a crystalline antibiotic elaborated by a Bacillus isolated from garden soil, proved to be a relatively simple polypeptide; when hydrolysed it yielded the five amino-acids: *l*-ornithine, *l*-proline, *l*-valine, *l*-leucine and *d*-phenylalanine in equimolecular proportions. When gramicidin-S was submitted to milder hydrolytic conditions, and the

products investigated in the usual way by partition chromatography, the following dipeptides were identified: *α-l*-valyl-*l*-ornithine; *l*-ornithyl-*l*-leucine; *l*-leucyl-*d*-phenylalanine; *d*-phenylalanyl-*l*-proline; as well as two tripeptides, probably: *α*-valyl-ornithyl-leucine and *d*-phenylalanyl-valyl-proline. It followed at once that the order of the amino-acids in the original compound was *α-l*-valyl-*l*-ornithyl-*l*-leucyl-*d*-phenylalanyl-*l*-prolyl-, the series occurring once or repeatedly in a cyclic peptide chain. It should be emphasised that all these results are obtained with quantities of material measured in micro- rather than milli-grams.

An incidental but very interesting point is that in gramicidin-S the amino-acid phenylalanine occurs not as the common *l*-form but as the "unnatural" *d*-variety. Gordon, Martin and Synge (*Biochem. J.*, 1943, **37**, 86, 313; see also Synge, *ibid.*, 1945, **39**, 355) have also carried out analyses of the antibiotics gramicidin and tyrocidin, produced by certain micro-organisms including *B. brevis*. Both these compounds are more complicated than gramicidin-S; the molecule of gramicidin, for instance, probably contains 24 amino-acid residues as well as ethanolamine, but they too contain some of their constituent amino-acids in the *d*-form. It looks as if the occurrence of "unnatural" configurations may be connected with their antibacterial action.

For details of the various methods whereby the dipeptides and tripeptides derived from these antibiotics were identified the original papers must of course be consulted and, indeed, with regard to the technique of partition chromatography in general the reader is strongly advised to consult the papers of Consden, Gordon, Martin and Synge (*loc. cit.*; see also *Biochem. J.*, 1943, **37**, 79, and Tristram, *ibid.*, 1946, **40**, 721) before attempting to use it himself, for there are many precautions to be taken in order to achieve the best results. The method is simple in principle, but needs some care and skill in its execution.

Other Applications of Partition Chromatography.—The methods of countercurrent distribution and partition chromatography are of course of general application, and with suitable modifications should be applicable to many problems in the field of biochemistry and elsewhere. The column technique has already been applied by Elsden (*Biochem. J.*, 1946, **40**, 252) to the identification and estimation of the fatty acids, acetic, propionic and butyric formed from cellulose by fermentation in the ruminant's stomach. The analysis of natural penicillin, which as is now well-known consists of various closely related compounds, has been developed by Goodall and Levi (*Nature*, 1946, **158**, 675), making use of one-

dimensional filter-paper chromatography. Here, the presence of the separated penicillins could not be conveniently demonstrated by a colour reaction; instead use was made of the bacteriostatic power of these compounds for the purpose of discovering their presence. The methods of partition chromatography are likely to become routine analytical procedures for both qualitative and quantitative work, and because of the extremely small quantities of material needed they are likely to make possible big advances, not only in the field of protein structure but in many other branches of science.

GEOLOGY. By G. W. Tyrrell, A.R.C.Sc., D.Sc., F.R.S.E., The University, Glasgow.

Igneous Petrography, North America and Africa: Petrology and Earth Structure.—Within the last fifteen years Professor M. P. Billings and a large number of his colleagues have been investigating the geological structure and petrology of New Hampshire, and have reached important conclusions on the mechanism of igneous intrusion in that State and elsewhere. The combined work has now reached the stage of generalisation and the present position is set forth in three general papers: M. P. Billings, "Ring-dikes and their Origin," *Trans. N.Y. Acad. Sci.* (II), **5**, 1943, 131–44; M. P. Billings, "Mechanics of Igneous Intrusion in New Hampshire," *Amer. Journ. Sci.*, **243-A** (Daly Volume), 1945, 40–68; M. P. Billings and N. B. Keevil, "Petrography and Radioactivity of Four Palæozoic Magma Series in New Hampshire," *Bull. Geol. Soc. Amer.*, **57**, 1946, 797–828. Professor Billings remarks: ". . . it seems probable that New Hampshire contains a greater variety of large intrusive forms than any area of equal size in the world."

The plutonic masses have been injected into meta-sedimentary and meta-volcanic rocks ranging in age from Ordovician (?) to Lower Devonian which have been intensely folded and regionally metamorphosed, mainly in the great Acadian orogeny of the Middle Devonian. Four magma series of distinctive petrographical characters were intruded during the Palæozoic: the Highlandcroft magma series in the late-Ordovician (?); the Oliverian magma series of approximately the Middle Devonian, and injected just before the Acadian movements; the New Hampshire magma series of the Middle or late-Devonian, and partly synchronous with, partly later than, the Acadian disturbance; and finally, the White Mountain magma series, younger than the Acadian orogeny, and probably Mississippian in age.

The petrographical characters and radioactivity of each of these magma series are given in Billings and Keevil's paper cited above. The syntectonic New Hampshire magma series occurs as great sheets, lenses and stocks, forcefully injected into the older formations. Some apparently plutonic masses have been formed by the "atomic" (metasomatic) replacement of older formations. Others, such as the Oliverian domes, oval-shaped cores of plutonic rocks ranging from granodiorite, through quartz-monzonite, to granite, possess a foliation which dips outwards in all directions, and appear to be comparable in some respects with laccoliths.

The most interesting intrusions to British geologists, however, are those of the White Mountain magma series which are characterised by ring-dikes, stocks, and a batholith. No fewer than thirty-six ring-dikes have now been described in New Hampshire. They range in composition from monzonite to quartz-syenite, and the suite has a definitely alkaline cast. The magmas have been injected into arcuate and circular vertical fracture zones by piecemeal stoping and related mechanisms; but cauldron subsidence, although present in some of the ring-dikes, is not essential for their formation. The stocks, mainly of biotite-granite, were emplaced by underground cauldron-subsidence. These ring-dikes obviously recall those of the Tertiary in the classic region of the Western Isles of Scotland; but, with their vertical contacts, they appear to resemble more closely the cauldron-subsidences of Glen Coe and Ben Nevis type.

The recent memoirs on which the above conclusions have been founded are: R. W. Chapman and C. A. Chapman, "Cauldron Subsidence at Ascutney Mountain, Vermont," *Bull. Geol. Soc. Amer.*, **51**, 1940, 191–212. A. Quinn and G. W. Stewart, "Igneous Rocks of the Merrymeeting Lake Area of New Hampshire," *Amer. Min.*, **26**, 1941, 633–45; J. B. Hadley, "Stratigraphy, Structure and Petrography of the Mt. Cube Area, N.H.," *Bull. Geol. Soc. Amer.*, **53**, 1942, 113–76; C. A. Chapman, "Intrusive Domes of the Claremont-Newport Area, N.H.," *ibid.*, 889–916; R. W. Chapman, "Ring Structures of the Pliny Region, N.H.," *ibid.*, 1533–68; A. Quinn, "Magmatic Contrasts in the Winnepesaukee Region, N.H.," *ibid.*, **55**, 1944, 473–96; C. A. Chapman, M. P. Billings, and R. W. Chapman, "Petrology and Structure of the Oliverian Magma Series in the Mt. Washington Quadrangle, N.H.," *ibid.*, 497–516; C. J. Roy and J. Freedman, "Geology of the Pawtuckaway Mountains," *ibid.*, 905–20; F. C. Kruger, "Structure and Metamorphism of the Bellows Falls Quadrangle of New Hampshire and Vermont," *ibid.*, **57**, 1946, 161–206.

R. J. Colony and H. A. Blank describe "Unusual Lamprophyre Dikes in the Manhattan Schists of New York City" (*Bull. Geol. Soc. Amer.*, **54**, 1943, 1693–1712) as amphibole-apatite-minettes. The dikes are from a few inches to 10 ft. in thickness, and carry numerous xenoliths of schist and gneiss. A possible relation is suggested between these dikes and the nepheline-syenite of Beemerville, N.J.

A large stock of alkaline rocks, mainly litchfieldite (albite-nepheline-syenite), at Blue Mountain, Ontario, has been studied by M. L. Keith (*Bull. Geol. Soc. Amer.*, **50**, 1939, 1795–1826). Age determinations based on radioactivity have shown that the litchfieldite (early Pre-Cambrian) is of the order of 500 million years older than the adjacent granite batholith (Late Pre-Cambrian), thus precluding the possibility of a genetic relation between them. On this and on the lack of evidence of desilication by limestone the conclusion is based that the limestone syntexis theory of Daly is not valid for this intrusion and probably not for the Bancroft alkaline petrographical province as a whole.

The "Audubon-Albion Stock, Boulder Co. Col.," described by E. E. Wahlstrom (*Bull. Geol. Soc. Amer.*, **51**, 1940, 1789–1820), is a composite intrusion consisting mainly of monzonite. It is injected into Pre-Cambrian metamorphic rocks, the sequence of intrusion being syenogabbro (oldest), monzonite, quartz-bearing monzonite, syenite and granite. The syenogabbro is rich in potash, and is correlated with neighbouring basalts of the early Eocene. The monzonite probably formed from the syenogabbro by crystal fractionation, but the later differentiates arose mainly by complex processes involving assimilation, syntexis, and transfer of materials by mobile, fluid-rich alkaline solutions.

Another region of ring-dike intrusion in North America is the Northern Quitman Mountains, Trans-Pecos, Texas, of which the geology is described by R. M. Huffington (*Bull. Geol. Soc. Amer.*, **54**, 1943, 989–1048). The Quitman pluton of quartz-monzonite and diorite has a discontinuous elliptical outcrop around volcanic rocks, and is interpreted as a ring-dike analogous to those of New England and Western Scotland.

A "Replacement Aplite Breccia" from Cornucopia, Oregon, has been described by G. E. Goodspeed and R. E. Fuller (*Journ. Geol.*, LII, 1944, 264–74). A brecciated zone in granodiorite shows that the fragments grade into an aplite matrix. It is believed that hydrothermal solutions rich in silica pervaded the coarse cataclastic zone, and the neighbouring crushed and broken rocks which were susceptible to metasomatic replacement. Thus the

granodiorite fragments were wholly or in part made over into aplite.

East Central Africa, especially on the borders of Uganda and the Belgian Congo in the neighbourhood of the Great Rift Valley (western), has lately provided some remarkable suites of igneous rocks, many of which have been described by Professor A. Holmes. These lava fields of the Western Rift range from undersaturated potash-rich types free from feldspar (Toro-Ankole field) through intermediate types such as leucite-basanites and basanitoid trachybasalts (Birunga field) to true olivine-basalts of various types such as characterise the great lava fields south of Lake Kivu. The last-named have been described by A. Holmes (*Geol. Mag.*, LXXVII, 1940, 89–101). Many of the rocks have recently been described by Belgian petrologists. They are dominantly basaltic and nearly all olivine-bearing; but there are subordinate trachytic types ranging from trachyandesites to phonolites.

In view of Bowen's opinion that some of the South Kivu basalts, like the trachybasalts of North Kivu, are probably potash-rich, Holmes has had two new analyses made of a normal olivine-basalt and an olivine-rich essexite-basalt. They turned out to be unusually poor in potash by any standard, and strikingly so in contrast with many occurrences in the Western Rift.

The study of "A Suite of Volcanic Rocks from South-west Uganda containing Kalsilite (a polymorph of $KAlSiO_4$)," by A. Holmes (*Min. Mag.*, **26**, 1942, 197–217), has shown that these lavas contain *kalsilite*, a new mineral which is a polymorph of kaliophilite, and was at first thought to be that mineral. Some of the rocks, besides being highly potassic, are also ultrabasic. They resemble olivine-rich ankaratrites or melanocratic olivine-nephelinites, with the difference that the nepheline- or kaliophilite-like mineral is really kalsilite. Other types contain leucite, biotite, or melilite, in addition. The term *mafurite* is proposed for a new rock type consisting of olivine, pyroxene, kalsilite, perofskite and ores; some varieties contain leucite, biotite, or melilite in some quantity. Mafurite, and the closely related lavas *katungite* and *ugandite*, are regarded as rheomorphic products due to the action of ultrabasic magma on rock material belonging to the biotite-peridotite—biotite-pyroxenite—glimmerite suite.

Venanzite is a lava consisting essentially of melilite, leucite, olivine, and a little phlogopite, from near San Venanzo, North Italy. In mafurite from Uganda (see last paragraph) A. Holmes has detected "A Heteromorph of Venanzite" (*Geol. Mag.*, LXXIX, 1942, 225–32) in which pyroxene and kalsilite take the place of part

of the melilite and leucite. The African heteromorph, however, is poorer in olivine and pyroxene, richer in melilite and leucite, than normal mafurite.

A. D. Combe and A. Holmes discuss "The Kalsilite-bearing Lavas of Kabirenge and Lyakauli, South-west Uganda" (*Trans. Roy. Soc. Edin.*, LXI, Pt. II, 1945, 359–79), Combe dealing with their geological setting and Holmes with petrology. The lavas are all potassic ultrabasic types containing various combinations of the minerals augite, melilite, leucite (or leucitic glass), and kalsilite. The four chief rock types are described as ugandite, mafurite, katungite, and kalsilite-katungite, but there are some transitional varieties. The lavas carry numerous xenoliths of granite (transfused —see next paragraph) and cognate xenoliths of pyroxenite, biotite-pyroxenite, biotite-augite-peridotite, and "glimmerite" (biotite-rock). The evidence indicates that these extraordinary lavas have resulted from partial incorporation, with or without preliminary transfusion, of (1) sub-volcanic rocks of the biotite-pyroxenite—peridotite group, and (2) granitic and other sialic crustal material, by potash-rich ultrabasic magma.

A. Holmes gives a complete description of the "Leucitized Granite Xenoliths from the Potash-rich Lavas of Bunyaruguru, South-west Uganda" (*Amer. Journ. Sci.*, **243–A** (Daly Volume), 1945, 313–32), mentioned in the previous paper. Granitic and other xenoliths enclosed in potassic ultrabasic lavas have suffered an extraordinary metasomatism by transfusion in progressive stages, which has produced leucite, or even leucitite and olivine-leucitite in extreme cases. From the enclosing mafurite magma K_2O, cafemic oxides, TiO_2, H_2O and CO_2, were carried differentially into the xenoliths, from which there was a compensatory expulsion of SiO_2, Na_2O, and some Al_2O_3.

"Ring Structures with Carbonate Cores in Southern Rhodesia" have been found by F. P. Mennell (*Geol. Mag.*, LXXXIII, 1946, 137–41). The rings are composed of nordmarkite, syenite, nepheline-syenite, shonkinite, ijolite, jacupirangite, with inclusions of coarse structureless masses of carbonates, magnetite-rock, and apatite-rock —in fact, identical with the occurrences at Fen (Norway), Alnö (Sweden), Afrikanda (Kola Peninsula), Iron Hill (Col.), and several others. Dr. F. Dixey has commented on the above discovery (*Geol. Mag.*, LXXXIII, 1946, 289–91) and compares the Rhodesian occurrences with those in Nyasaland and Uganda.

J. Verhoogen has described the geology and petrography of the kimberlite pipes, twenty-four in number, of the Kundulungu Plateau in Katanga ("Les Pipes de Kimberlite du Katanga," *Ann.*

d. Sérv. des Mines. Comm. Spéc. Katanga, Brussels, IX, 1940, p. 46). One of them, Talala, is the largest in Africa. The pipes are probably of Cretaceous age. The kimberlite is generally of the "basaltic" type; only one occurrence of the micaceous or lamprophyric type is known. There is a large content of olivine, both magnesian and calcic. At least a part of the abundant serpentine is anterior to the formation of the calcic olivine, and is thought to be of magmatic and not deuteric origin. Some of the calcite present is thought to be primary. The kimberlites contain abundant inclusions, mostly granulites, some of which resemble members of the charnockite series. These provide information as to the probable constitution of the basement of the Kundulungu Plateau.

"The Hangnest Dolerite Sill, S.A.," described by F. Walker and A. Poldervaart (*Geol. Mag.*, LXXVIII, 1941, 429–50), is 500 ft. thick and consists of a coarse dolerite, the lower two-thirds of the sill being orthopyroxene-bearing. The composition of the associated Karroo sediments (siltstone) is such that they easily underwent mobilisation with the addition of soda and cafemic oxides as "emanations" from the dolerite magma. The product of this metasomatism is a granophyric rock of very distinctive appearance which forms rheomorphic veins and dikes. This association of dolerite, granophyre, and siltstone is widespread in the Karroo.

Petrology and Earth Structure.—The joint paper of W. Q. Kennedy and E. M. Anderson on "Crustal Layers and the Origin of Magmas" (*Bull. Volc.* (*Naples*), Sér. II, Tom. III, 1938, 23–82) is of fundamental importance in petrological theory. Its purpose is to explore the connection of igneous activity with geophysics and crustal tectonics. Kennedy deals with the petrological aspects of the problem, and brings forward the fruitful concept of volcanic and plutonic associations. The former includes lavas, vent intrusions, and all intrusive masses which may be coarse-grained and "plutonic" in habit, which are genetically related to a cycle of volcanic activity and originate in the same magmatic source. Plutonic associations comprise the great subjacent batholiths and stocks together with the many minor intrusions that accompany them. Volcanic associations stem mainly from basaltic magma; plutonic associations from the granodiorite kindred. Kennedy also discusses the two lines of descent, olivine-basalt—phonolite (alkaline), and tholeiite—rhyolite (calc-alkaline), of the volcanic association, and shows that the former is most likely to arise in non-orogenic and the latter in orogenic regions.

Anderson discusses the geophysical data as applied to the magma problem. He considers the questions of crustal tempera-

tures, seismic data, etc., and comes to the conclusion that primary fusion of the granitic layer can only take place in orogenic regions. The locus of origin of olivine-basalt is left doubtful; but tholeiite magma is considered quite definitely to come from the P* layer of the seismologists.

In his presidential address to the Mineralogical Society of America, A. F. Buddington dealt with "Some Petrological Concepts and the Interior of the Earth" (*Amer. Min.*, **28**, 1943, 119–40). The concepts referred to are those of: "fractional crystallisation, fractional melting, the *systematic* nature of the variation which the great thick mafic stratiform sheets such as the Bushveld, Duluth and Stillwater have in common, and the necessity for providing a rational mechanism for the origin of such magmas as are considered primary, or in the words of Loewinson-Lessing, proto-magmas." The nature and variations of meteorites are also dealt with in relation to the analogous terrestrial igneous rocks, and to petrology in general. Buddington believes that a layered earth is peculiarly suitable for the derivation of primary magmas, and uses E. M. Anderson's methods of procedure developed in the preceding paper. The discussion leads to a modification of current earth-models whereby a layer of bytownite-anorthosite at or near a depth of 25–30 km. is postulated, and probably a relatively thin vitreous peridotite or dunite shell rich in hydrogen and other volatiles, beginning at a depth of 60–80 km. and perhaps some hundreds of kilometres thick.

In his important paper "Meteorites and an Earth-model," R. A. Daly (*Bull. Geol. Soc. Amer.*, **54**, 1943, 401–56) discusses a topic related to those of the two previous papers. His central hypothesis is the old one that the earth is composed of materials of which meteorites provide samples. The paper summarises the principal observed facts on the nature of meteoric stones and irons, and gives the reasons for believing them to be fragments of a disrupted parental planet which belonged to the solar system, and therefore similar in composition to the earth. After a comparison of the earth with the assumed parental planet, a course of earth evolution is suggested which gives the following succession of shells from surface to centre: a true crust, the lithosphere; a thicker vitreous asthenospheric shell; a still thicker mesospheric shell; and a nickel-iron core, probably fluid and possibly behaving much like a gas. This suggestion is tested by reference to the discontinuities revealed by seismic studies, mean density, moment of inertia, radioactivity, and plasticity of the earth.

In the foregoing paper Professor Daly suggested that the astheno-

sphere was wholly vitreous and of peridotitic composition. New data on the effects of rising temperatures on the compressibility of liquids, glasses and crystalline solids from the Harvard laboratories have compelled him to revise his ideas. In a paper on the " Nature of the Asthenosphere " (*Bull. Geol. Soc. Amer.*, **55**, 1946, 707–26) he now suggests that the deeper and greater part of the thick, weak shell (asthenosphere) is peridotitic in composition, but in the physical condition of a two-phase mixture of dominant crystals and subordinate glass or, possibly, a gaseous solution in the critical state.

Basic to ultrabasic igneous rocks characterise the axes of geosynclines at an early stage of their development. Later on, when the geosynclinal sediments have been folded, granitoid rocks make their appearance in huge quantities. J. H. F. Umbgrove, in a paper on " The Relation between Magmatic Cycles and Orogenic Epochs " (*Geol. Mag.*, LXXVI, 1939, 444–50), which is difficult to summarise, attempts to correlate the above igneous cycle with the tectonic cycle of orogenic regions, and the layering of the earth's crust. Rhythmic thermal and magmatic events in the depths of the crust are said to produce alternating periods of expansion and contraction, and to cause the well-known sequence of magmatic types in orogenic regions.

In a second paper on " Magmatic Problems " the late F. Loewinson-Lessing (*Trans. Acad. Sci. U.S.S.R.*, 1939, pp. 1–18, Russian text, 18–24 English summary) dealt with the supposed connection between types or associations of igneous rocks with crustal movements, and comes to the conclusion that the idea of contrasted associations with kratogens and orogens, or with epeirogenic or orogenic movements, is fallacious. He believes that magmatic processes are connected only with vertical movements in both epeirogenic and orogenic phases. He also treated of the classification of igneous rocks, the criteria of orthomagmatic and paramagmatic rocks, and the problems of the origin of anorthosite and other monomineralic rocks.

H. H. Hess discusses the possibility of " A Primary Peridotite Magma " (*Amer. Journ. Sci.*, **35**, 1938, 821–44). It is accepted that some ultrabasic types are crystal accumulates from basaltic magmas as, for example, the contact-chilled peridotite and dunite dikes of Skye described by Harker and later by Bowen. This generalisation, however, has been extended to cover the origin of all ultrabasic types. Physical and chemical evidence, *e.g.* impossibly high magmatic temperatures, is mostly opposed to the possibility of primary ultrabasic magmas. At the same time the geological evidence is mostly in their favour. Dr. Hess concludes in favour

of primary ultrabasic magmas, which mainly occur as long narrow belts in orogenic zones, and promulgates a theory to explain their anomalous low temperatures and the apparent absence of effusive equivalents.

R. E. Fuller writes on "Gravitational Accumulation of Olivine during the Advance of Basaltic Flows" (*Journ. Geol.*, XLVII, 1939, 303–13). A surface depletion and a basal concentration of olivine above a chilled lower contact in Late Tertiary basaltic flows in Oregon, suggests that the olivine crystals gradually accumulated in a manner reminiscent of the deposition of sand in the foreset beds of a delta.

N. L. Bowen's important paper on "Phase Equilibria bearing on the Origin and Differentiation of Alkaline Rocks" (*Amer. Journ. Sci.*, **243–A** (Daly Volume), 1945, 75–89) deals with recent studies of equilibrium relations in the quaternary system Na_2O—CaO—Al_2O_3—SiO_2, which show that certain melts, crystallised non-fractionally, will give melilite, nepheline, and wollastonite; yet the same liquids, with fractional crystallisation will, in addition, give plagioclase, calcic at first but eventually highly sodic. Hence, by fractional crystallisation, may develop a series of differentiates which may be called melilite-nephelinite, tephrite and phonolite. In natural magmas a parallel series may be formed by similar processes. Continued fractionation at a later stage may give a concentration of a waterglass-like sodium silicate, along with water and other volatiles. The penetration of this residuum into aluminous country-rocks may give rise to nepheline and albite, and thus produce "igneous-looking" rock types similar to the parent intrusion.

S. J. Shand writes on "The Present Status of Daly's Hypothesis of the Alkaline Rocks" (*Amer. Journ. Sci.*, **243–A** (Daly Volume), 1945, 495–507). He is of opinion that neither absence of visible limestone at some localities, nor the absence of visible reaction at others, constitute disproof of Daly's hypothesis of "limestone-syntexis." Many observations show that foyaite can be generated from granite through desilication by limestone syntexis; that syenite and foyaite may be further desilicated to ijolite; and that basalt may give rise under similar conditions to theralite and melilite-rocks. Shand therefore maintains that Daly's hypothesis still holds the field.

BOTANY. By PROFESSOR W. H. PEARSALL, D.Sc., F.R.S., University College, London.

THE Presidential Address delivered by Sir William Wright Smith to the Royal Society of Edinburgh (*Year Book*, *R.S.E.*, 1946) dealt with the subject of plant invaders with particular reference to the flora of New Zealand. Long ago, both Hooker and Darwin had been impressed by the occurrence, particularly in alpine regions, of Scandinavian and Northern genera and, as they thought, even of Scandinavian species. Coupled with the extraordinary manner in which European species of plants had spread in New Zealand, there appeared to be some grounds for the idea that a northern flora had a particularly high penetrative and colonising power. The problem has continued to exercise the attention of botanists and other scientists even until the present time. Of recent years, a good deal has been added to our knowledge of these alien invaders, and H. H. Allan has recorded that the greatest enemies of a pastoralist in New Zealand are the indigenous and not the alien plants, and that the striking feature which now presents itself is not at all the aggressiveness of the aliens but the power of indigenous plant communities to prevent their entry. It is only where draining, cultivation and constant burning of forest, scrub and moorland and the grazing of a multitude of animals have made new edaphic conditions, which approximate to those of Europe that the European invaders seem to be able to some extent to become successful. Whatever may have, in the past, led to extension southwards of the north temperate flora, its dominance at the present time is discountenanced. Its chances in the southern climes are favourable only when man intervenes. There, in cultivated lands, the dice are loaded against the New Zealanders.

A similar result has perhaps been observed in some parts of Scotland, where on the whole the climate may not be unfairly compared with that of New Zealand. The extensive alien flora of Tweedside numbers as many as 348 species, of which 145 came from south of the Equator. These are almost all ephemeral and persist only from year to year by reason of farther arrivals. The same fugitive characteristics of alien species was observed by Thellung in his *La Flore Adventice de Montpellier*, where 800 aliens were recorded, of which only ten survived when the supply of new seeds was interrupted for twenty-five years. A similar answer was given also for some sub-tropical areas as, for example, Madagascar, where of 900 alien species only 1, *Adenostemma viscosum*, has gained a foothold in natural plant communities undisturbed by man.

In Scotland perhaps two factors go far to explain the non-success

of immigrants from New Zealand. In the first place the native flora of New Zealand does not contain any weeds of cultivation and, secondly, when New Zealand plants arrive in Scotland they have little chance of being introduced into virgin soil, except perhaps on the high mountains, in a few marshes and along the sea shores. Thus, few species from south of the Equator or from New Zealand have made much progress in Scotland and only 7 examples from Britain, of which 2 are from south of the Border, can be fairly considered to have become established in the last forty years. Perhaps the most widespread is *Epilobium alsinoides* A. Cunn., an Italian and New Zealand willow-herb possibly with *E. nummularifolium* and *E. pedunculare*, representing a single polymorphic species; *Mesembryanthemum edule* is established with *M. æquilaterale* in Cornwall and south Devon and is now said also to be established in Iona. *Galinsoga parviflora* Cav., whose name was corrupted in the London suburbs to Gallant Soldier, was first noticed near Kew in 1887 and is now very prevalent in the London district though not in Scotland. In the same category, but much less frequent, are *Acæna anserinifolia*, *Senecio smithii*, *Pernettya mucronata* and *Pratia angulata*. The examination of this problem further suggests that, even under approximately similar conditions, the native flora of any country seems to have that little extra which gains success from the invader. They may meet in the garden, but not outside. How many generations will the alien, even of the same genus, require to establish the adjustment which will enable it to succeed in a new site?

Two long papers have appeared dealing with the cytological and genetical characteristics of the genus *Solanum*, with particular reference to many wild and native cultivated diploid forms of potato. The investigations have been carried out by H. C. Choudhuri (*Trans. Roy. Soc. Edinb.*, LXI, 113, 1943, and *ibid.*, LXI, 119, 1944). The data recorded suggest that the primary basic number of chromosomes is 6, the haploid number in most of the species investigated being 12. Considerable quantities of data are given showing the frequency of univalent and bivalent fragments under various conditions, and there are also data showing the results of mating, of reciprocal crosses, as well as of the average number of seeds per berry and some observations of the characteristics of the pollen. This is essentially a detailed report for specialists.

Another genetical study dealing with potatoes comes from William Black, dealing with the inheritance of resistance by potatoes to two strains of blight (*Phytophthora infestans*). He had earlier shown (*Trans. Roy. Soc. Edinb.*, LXI, 137, 1943) that the reaction

of potatoes to the attacks of the disease is genetically controlled. It was further necessary to investigate the inheritance of resistance to strains of different types. Two strains were used, one of which is much more virulent than the other. Segregation of resistant and susceptible plants following infection with the two strains have been traced through several generations of hybrids bred from (*a*) *S. rybinii*, *S. demissum* and *S. tuberosum* and (*b*) *S. demissum* and *S. tuberosum*. The available evidence now indicates (*Proc. Roy. Soc. Edinb.*, B, LXII, 171, 1945) that resistance to blight is controlled by major genes upon which depend the major reaction, resistance, or susceptibility, and by minor genes which determine the degree of susceptibility in susceptible varieties and act as unidentified modifiers. Segregation of resistant and susceptible plants in the progenies shows a highly consistent excess of recessive individuals compared with the standard 1 : 1, 3 : 1, and 15 : 1 ratios. It is suggested that the excess of recessives may be due in part to chromosome homologies leading to multivalent formation and double reduction. In the material under discussion, however, the excess is largely due to the differential compatibility of gametes arising from residual incompatibility factors associated with the original " wild " material.

An approach to the problems of phyllotaxy has been made by D. A. Coult (*Journ. Linn. Soc. Bot.*, LVII, 109, 1946). He has examined some abnormal types of *Salvia* (*S. verbenaca* and *S. pratensis*) in which various modifications of the normal decussate leaf arrangement had taken place. Both species are somewhat similar in form and the modifications are of a generally similar type, in which sometimes pairs and single leaves alternate, and other times the stem is triangular or pentangular with somewhat irregular or even trimerous leaf arrangement. The examination of stem anatomy showed that the variations were associated with an increase in meristematic activity at certain points rather than with localised differential extension of tissues. The description of the actual facts is associated with an interesting detailed discussion of the nature of the causative factors in the light of Schoute's " binding factor " hypothesis and the supposition that hormone production is responsible for some of the observed growth effects.

An interesting paper on the ecology of the Black Beakrush, *Schœnus nigricans*, by S. R. Gauday, has appeared in *Bol. Soc. Broteriana*, XIX, 373, 1945. This describes the occurrence of Schœnus as a dominant in two sorts of plant community, one in which it is associated as succeeding reed swamps containing *Phragmites* and *Cladium mariscus*, and the second in which it occurs

in succession to salt marsh plants and associated with species such as *Juncus maritimus* and other types of the higher salt marsh. In both habitats the soil has not only a high water content but is also slightly alkaline, with not less than 10 per cent. of calcium carbonate and a comparatively unimportant salt content. In Portugal there appears to be nothing comparable to the occurrence of Schœnus on bog peats such as is observed in the west of Ireland and the Western Highlands. It is, however, associated in some situations with the presence of considerable quantities of gypsum in the soil.

Another paper of considerable importance from Portugal is by D. De Castro (*Bol. Soc. Broteriana*, XIX, 525, 1945). This is a systematic and partly genetical study of species of *Echinospartum* and *Ulex* found in the Iberian peninsula. Chromosome numbers are given for most of the species mentioned including *Ulex minor*, *U. gallii* and *U. europæus*. Numbers ($2n$) were respectively 32, 80, and 64 to 96, The latter figures refer to two sub-species, Sspp. *latebracteatis* and *L. borealis*, and on the basis of the cytological differences it is suggested that these should be raised to the rank of species, while the hypothesis is put forward that *U. gallii* is a hybrid of these two sub-species. The basic chromosome number of 8 is suggested for the European Genisteæ, and details of geographical distribution are also given for most of the considerable number of species included in the survey.

PLANT PHYSIOLOGY. By Professor Walter Stiles, Sc.D., F.R.S., The University, Birmingham.

Plant Hormones.—A very large number of papers have appeared in recent years on plant hormones, and it is only possible here to refer to a representative selection of these and indicate current trends of research.

Since the isolation of the three hormones auxin *a*, auxin *b* and heteroauxin, and the establishment of their chemical constitution by Kögl and his collaborators, many substances allied in constitution to these have been examined, in order to determine whether they have growth-regulating properties resembling those of the auxins. This line of enquiry has culminated in an investigation by H. E. Thompson, C. P. Swanson and A. G. Norman assisted by a number of other workers ("New Growth-Regulating Compounds, I. Summary of Growth-Inhibitory Activities of some Organic Compounds as Determined by Three Tests," *Bot. Gaz.*, **107**, 476–507, 1946) in which 1060 organic compounds were examined from the

point of view of their growth-regulating activity. Three methods of testing were used. The first method depended on the retardation of growth of the primary root of maize seedlings resulting from germinating the grains in presence of an aqueous solution of the substance in a concentration of 10 p.p.m. (parts per million). In the second test a drop (0·02 ml.) of an aqueous solution containing $4\mu g$. of the material was placed on the upper surface of the leaf of a kidney bean seedling and the resulting inhibition of growth was estimated. The third method depended on a somewhat similar test with " oil " as the solvent instead of water. More than 100 of the substances examined were found to have high growth-regulating activity.

Much work has been carried out during the last decade on the effect of auxins and related substances on various plant activities. Among recent investigations of this kind may be mentioned that of J. Berger, P. Smith and G. S. Avery on the effect of indoleacetic acid on respiration (" The Influence of Auxin on Respiration of the Avena Coleoptile," *Amer. J. Bot.*, **33**, 601–4, 1946). The coleoptiles of oat seedlings grown under controlled conditions, and after removal of the tip and enclosed foliage leaf, were cut into segments about 4 mm. long, immersed in solutions of indoleacetic acid for about 15 hours and the respiration rate compared with that of controls not treated with auxin. It was found that the respiratory intensity of coleoptile tissue treated in this way with a solution of 10 mg. indoleacetic acid per litre was about 35 per cent. higher than that of the untreated control.

The effect of growth hormones on the hydrolysis of starch has been examined by S. C. Bausor (" Effects of Growth Substances on Reserve Starch," *Bot. Gaz.*, **104**, 115–21, 1942). He found that when cuttings of tomato plants supplied with a mineral nutrient solution containing sucrose, maltose, fructose, glucose or lactose, were treated with indoleacetic acid or β-naphthoxyacetic acid in lanolin and then kept in the dark, there resulted a depletion of the starch, whereas controls supplied with the same solution, but without the growth substance, still had much starch after 6 days. On the other hand, 0·02 or 0·002 per cent. aqueous solutions of indoleacetic acid inhibited amylolysis in thin sections of tomato and bean stems. Reasons for the different effects in intact stems and in sections is not clear.

More information on this subject is provided by H. C. Eyster, who has examined the effect of indole-3-propionic acid and three other growth substances on diastatic action (" Auxin Action," *Science*, **97**, 358–9, 1943 ; " Effect of Auxins on the Action of

Diastase *in vitro*," *Plant Physiol.*, **21**, 68–74, 1946). By the use of the iodine test for starch it was established that presence of the growth substance in concentrations of 25 and 50 p.p.m. retarded the hydrolysis of starch by free diastase, but if diastase adsorbed on charcoal was used the action of the enzyme was accelerated. Eyster suggests that there are two phases in the action of auxin on adsorbed diastase, the first phase involving the release of the enzyme from the adsorbent, while the second phase is concerned with the actual action of the auxin on the enzyme. In the first phase auxin accelerates the release of the enzyme and so tends to increase the rate of enzyme action ; in the second phase, the auxin retards the action of the freed enzyme. The auxin may thus be growth-promoting or growth-retarding according to the relative effects of the two phases. Eyster concludes that the interaction of auxins and enzymes at colloidal surfaces in the cell may be similar to the interaction of auxin and diastase on the surface of charcoal.

P. C. Marth ("Effects of Growth-Regulating Substances on Shoot Development of Roses during Common Storage," *Bot. Gaz.*, **104**, 26–49, 1942) examined the effects of a number of growth substances, including indoleacetic acid, on rose bushes in storage. Among the effects noted was an inhibition of the sprouting of vegetative buds, which thus remain dormant. There was also observed a conservation of reserve starch. This might be ascribed either to direct inhibition of amylolysis or to inhibition of growth which would, of course, check the utilisation of reserves.

C. L. Hamner and P. C. Marth have tested the effects of several growth substances, including indolebutyric acid, on the rooting of cuttings of *Solidago leavenworthii* ("Effects of Growth-Regulating Substances on Propagation of Golden-rod," *Bot. Gaz.*, **105**, 182–92, 1943). They report that the rooting of cuttings of the stolon soaked for 3 hours in a 10 or 50 p.p.m. solution of indolebutyric acid was somewhat better than that of untreated controls, while dusting with this and some other growth-regulating substances held in talc also brought about an increase in root production. A greater production of roots by stem cuttings also was brought about by soaking these for 3 hours in a 25, 50 or 100 p.p.m. solution of indolebutyric acid.

Results obtained in the past on the effect on growth by treating seeds with growth substances have been contradictory. Now W. S. Stewart and C. L. Hamner ("Treatment of Seeds with Synthetic Growth-Regulating Substances," *Bot. Gaz.*, **104**, 338–47, 1942), have tested the effect on subsequent growth by treating seeds of radish and oat, planted in pots in a greenhouse, with indoleacetic acid and other growth substances in a wide range of

concentrations. They found no significant increase in growth resulted from the treatment. Field experiments carried out with the same and seven other crop plants produced the same negative result. However, R. W. Allard, H. R. Derose and C. P. Swanson ("Some Effects of Plant Growth-Regulators on Seed Germination and Seedling Development," *Bot. Gaz.*, **107**, 575–83, 1946) found that 2, 4-dichlorophenoxyacetic acid retarded germination and brought about abnormalities in the growth of seedlings of a number of species including kidney beans, wheat and oats.

A number of investigators have reported on the favourable effect on the setting of tomato fruit as a result of treatment with growth-regulating substances. Among these may be mentioned F. G. Gustafson ("β-Naphthoxyacetic Acid as an Inductor of Parthenocarpy in Tomatoes," *Proc. Amer. Soc. Hort. Sci.*, **40**, 387–9, 1942), and J. W. Mitchell and M. R. Whitehead ("Effects of Vaporous Naphthoxyacetic Acid on Development of Tomato Fruits, with Special Reference to their Vitamin C Content," *Bot. Gaz.*, **104**, 362–5, 1942). Gustafson applied the growth substance as a paste smeared on the cut surface, while Mitchell and Whitehead subjected the plants to the vapour of the substance in a closed room in which the plants remained overnight. Treatment reduces seed development, although the extent of the inhibition of seed production depends on the time of the treatment in relation to pollination. Thus Mitchell and Whitehead found that the greatest effect was obtained when treatment took place at the time of pollination or during the preceding 5 days, the number of seedless fruits developing then amounting to 50–70 per cent. of the whole. By repeatedly subjecting plants to the vapour these workers succeeded in raising the percentage of seedless fruits in some instances to 98 per cent. Determination of the vitamin C content of fruit from treated and untreated plants showed that the treatment brought about no reduction in the vitamin content.

The pineapple in cultivation produces seedless or parthenocarpic fruit, but H. E. Clark and K. R. Kerns ("Effects of Growth-Regulating Substances on a Parthenocarpic Fruit," *Bot. Gaz.*, **104**, 639–44, 1943) found that spraying pineapple plants with a solution of α-naphthalene-acetic acid after the floral primordia had differentiated brought about a definite increase in the size and weight of the fruit.

J. W. Mitchell and P. C. Marth ("Effects of 2, 4-Dichlorophenoxyacetic Acid on the Ripening of Detached Fruit," *Bot. Gaz.*, **106**, 199–207, 1944) have examined the effect of the synthetic growth substance 2, 4-dichlorophenoxyacetic acid on the ripening of a number of fruits (apples, bananas, pears, peppers, persimmons and

tomatoes) detached from the plant. Of these different fruits they found that apples, bananas and pears all ripened more rapidly as a result of the treatment, whereas, judging from the change in colour, the treatment had no effect on the rate of ripening of peppers, persimmons and tomatoes. In bananas application of the iodine test for starch showed that amylolysis proceeded at a more rapid rate as a result of the treatment.

As regards the effect of growth-regulators on shoot development a very considerable piece of work has been carried out by C. E. Ostrom on forest trees ("Effects of Plant-Growth Regulators on Shoot Development and Field Survival of Forest-Tree Seedlings," *Bot. Gaz.*, **107**, 139–83, 1945). The species examined included a number of pines (*Pinus resinosa*, *P. pungens*, *P. tæda*, *P. rigida*, *P. ponderosa*, *P. echinata*), white ash (*Fraxinus americana*) and the tulip tree (*Liriodendron tulipifera*). A number of growth substances were used, including naphthalene-acetic acid, and the treatment was applied in various concentrations and in various ways as, for instance, by dipping in a solution, spraying, and exposing to a vapour. Treatment was applied in the nursery bed, before storage or before planting out. It was found possible to stop needle development of pine seedlings and in some species to inhibit the development throughout the season. The comparatively high concentrations required to inhibit growth were, however, near those toxic enough to kill the trees. The reduction of shoot growth in *Pinus resinosa* brought about by treatment with growth regulators was not accompanied by greater drought resistance. Spraying and treatment with vapour could also bring about an inhibiting effect on the development of etiolated shoots and a furthering of root development in seedlings of *Fraxinus americana* in storage. Treatment of trees before planting out did not result in any improvement in the survival of pines.

Experiments on the effect of indolebutyric acid on the development of the seedlings of a number of trees, particularly eastern red oak (*Quercus borealis maxima*) have been made by T. E. Maki and H. Marshall ("Effects of Soaking with Indolebutyric Acid on Root Development and Survival of Tree Seedlings," *Bot. Gaz.*, **107**, 268–76, 1945). Here also there was little evidence of increase in survival resulting from treatment with the indolebutyric acid and relatively high concentrations were definitely toxic. There was, however, a very definite increase in root growth, but this was associated with increase in mortality of the seedling.

Several investigators have shown that growth-regulators can bring about changes in form such as curvatures of the stem, dis-

tortions of petioles and production of galls. Some of these effects are described by J. M. Beal ("Some Telemorphic Effects induced in Sweet Pea by Application of 4-chlorophenoxyacetic acid," *Bot. Gaz.*, **105**, 471–4, 1944; "Further Observations on the Telemorphic Effects of Certain Growth-Regulating Substances," *Bot. Gaz.*, **106**, 165–78, 1944). Since these effects are often produced at some distance from the place of application of the growth-regulator they are described by Beal as telemorphic.

It will be clear from what has already been written that growth-regulators in sufficient concentration can exert a toxic action. Different species can be affected to different extents by the same substance and this differential effect can be utilised in removing weeds from a crop. Recently much work has been done in testing the effects of different growth-regulators as weed-killers or herbicides. R. E. Slade, W. G. Templeman and W. A. Sexton (*Nature*, **155**, 497, 1945) mention an experiment carried out in 1940 in which oats and charlock were sown together and received an application of 25 lb. of α-naphthylacetic acid, with the result that the charlock was killed while the oats were only slightly affected and recovered completely. The same workers report that other cereals behaved similarly to oats, while plantain (*Plantago major*) and yarrow (*Achillea millefolium*) behaved like charlock. They also tested the herbicidal action of a number of synthetic growth-regulators and found that 4-chloro-2-methyl-phenoxyacetic acid was particularly active. Another substance found to be a strong herbicide is 2, 4-dichlorophenoxyacetic acid (P. C. Marth and J. S. Mitchell. "2, 4-Dichlorophenoxyacetic Acid as a Differential Herbicide," *Bot. Gaz.*, **106**, 224–32, 1944; C. L. Hamner and H. B. Tukey, "Selective Herbicidal Action of Midsummer and Fall Applications of 2, 4-Dichlorophenoxyacetic Acid," *Bot. Gaz.*, **106**, 232–45, 1944; P. S. Nutman, H. G. Thornton and J. H. Quastel, "Inhibition of Plant Growth by 2, 4-Dichlorophenoxyacetic Acid and other Plant Growth Substances," *Nature*, **155**, 497, 1945).

Work by the various investigators cited shows that by the use of these herbicides such weeds as corn buttercup (*Ranunculus arvensis*), field poppy (*Papaver Rhœas*), corn marigold (*Chrysanthemum segetum*), corn spurry (*Spergula arvensis*), dandelion (*Taraxacum dens-leonis*) and pennywort (*Hydrocotyle rotundifolia*) can be removed from a cereal crop. Much activity is at present being shown in investigating the effects of 2, 4-dichlorophenoxyacetic acid on various plant species and under various conditions.

Finally, reference may be made to a paper by S. A. Gordon on the state in which auxins occur in plants ("Auxin-Protein Complexes

of the Wheat Grain," *Amer. J. Bot.*, **33**, 160–9, 1946). The view is accepted that in living tissues auxins are bound with other groupings and in particular with proteins. This is indicated in the wheat grain, since both endosperm and embryo meals after digestion with trypsin have an auxin content about three or four times as high as that of undigested controls. The various proteins of the wheat grain, glutenin, gliadin, α-glutelin, β-glutelin, globulin, leucosin and proteose, were extracted and their growth activity found to be zero by the Avena test. They were then subjected to the action of trypsin under controlled optimum conditions of temperature and *p*H, and the amount of free auxin left after digestion of the protein determined. A considerable amount of auxin was obtained in this way from the leucosin, globulin and proteose of the embryo, less from the gliadin, glutenin and α-glutelin of the endosperm, while none was obtained from the β-glutelin. From electrodialysis experiments Gordon concludes that the auxin is held to the protein by adsorption or as an unstably bound electrolyte.

ENTOMOLOGY. By A. D. Lees, M.A., Ph.D., Agricultural Research Council, Unit of Insect Physiology, Cambridge.

Mouth-parts and Feeding Mechanisms.—Future writers of text-books on medical entomology will no doubt draw freely from the monograph by R. E. Snodgrass on the feeding apparatus of biting and sucking insects affecting man and animals (*Smithsonian Misc. Coll.*, 1944, **104**, No. 7). The scope of this publication is wide and is based on broad evolutionary considerations. The sucking lice (Anoplura) are approached by way of the biting lice (Mallophaga) and the booklice (Corrodentia): and the Thysanoptera serve as an introduction to the Hemiptera. The Diptera, particularly disease-carrying species, take pride of place however. Particular attention is given to the arrangements of the muscles actuating the biting and piercing armature, inasmuch as they serve as guides both to the mechanisms of feeding and to the homologies of the mouth-parts themselves. In a later publication devoted to the skeletal anatomy of fleas (*Smithsonian Misc. Coll.*, 1946, **104**, No. 18) the same author reconsiders the mouth-parts and feeding mechanisms in these insects. Certain of the flea organ systems, for example the male intromittent organ, are of extraordinary complexity.

The mouth-parts of the weevil *Calandra granaria* exhibit many structural and functional modifications in connection with their situation at the tip of an elongated rostrum (R. Dennell, *Phil. Trans. B.*, 1942, **231**, 247). They are actuated by long tendons in the rostrum, the muscles lying entirely within the head capsule. The cutting off of

particles of grain, their trituration and subsequent passage into the pharynx can be related to the mechanics of the mandibles and maxillæ. Attached to the bases of the mandibles and lying in the pharynx are long bracons armed with recurved spines. These move with the mandibles and, assisted by pressure from the roof, are instrumental in thrusting the food particles down the pharynx. The proventriculus in this insect is lined by a number of grooved plates provided with numerous fine setæ. It functions as a sieve, retaining food in the crop until partially digested by the mid-gut digestive juices.

That filtration is not the original function of the proventriculus in the Coleoptera is shown by F. Balfour-Browne (*J. Roy. Micros. Soc.*, 1944, **64**, 68) in a study of the evolution of this organ in the Adephaga. In the more primitive Hydradephaga the proventriculus is a crushing organ made up of overlapping " apron " lobes and " crusher " plates, the latter bearing formidable teeth. In more advanced forms, like the Dytiscidæ, the chitinous teeth disappear and the proventriculus appears to serve only as a filter. This is also its function in most Geodephaga where the occurrence of a definite crushing apparatus is rare.

INSECT DIETETICS.—The basic food requirements of insects, and particularly their vitamin requirements, have recently received much attention. The dietetics of a number of insects infesting stored products are examined in a series of papers by G. Fraenkel and M. Blewett. Sterols were found always to be essential for growth (*Biochem. J.*, 1943, **37**, 692). Many flour insects, such as *Tribolium*, *Silvanus*, *Ptinus* and *Ephestia*, grow on a diet of either animal or vegetable origin and can utilise cholesterol, sitosterol or ergatosterol. The hide beetle *Dermestes* can only grow if cholesterol is present—a circumstance which may limit the beetle to food of animal origin. The need for carbohydrates in the diet varies in different insects. For *Ephestia kuehniella*, *Sitodrepa* and *Silvanus*, insects which infest all kinds of cereal products and sometimes dried fruit, carbohydrates are essential for growth. Other insects, such as the tobacco beetle *Lasioderma*, are much less exacting in this respect (*J. exp. Biol.*, 1943, **20**, 28). The carbohydrate requirements of *Ephestia* are particularly high, the moths thriving on a diet containing up to 80 per cent. glucose. But, whereas glucose can be successfully replaced by starch in the diet of *E. kuehniella*, two other species, *E. elutella* and *E. cautella*, cannot grow in its absence. In infested flour mills the latter species may be feeding mainly on the fragments of the wheat germ which are rich in glucose ; *E. kuehniella* also feeds on the endosperm of the grain (*J. exp. Biol.*, 1946, **22**, 162).

Other fat-soluble substances besides sterols are necessary for the growth of the moths *Ephestia* and *Plodia*. These are present in wheat germ oil. If this is deficient, growth is slow and the moths fail to emerge or do so with only a few scales on the wings. In this latter condition the scales appear to be fully formed but adhere to the inside of the pupal case (*J. exp. Biol.*, 1946, **22**, 172). . The active principle of the saponifiable fraction of the germ oil, which is responsible for emergence and good scales, is linoleic acid. A constituent of the unsaponifiable fraction is also necessary for the growth of the larvæ. This may be vitamin E, which functions as an antioxidant stabilising linoleic acid.

It has been known for many years that certain insects such as *Tribolium* develop much more rapidly on wholemeal flour than on highly milled patent flour; and it has been suggested that this effect is traceable to a deficiency in the patent flour of vitamins of the B-complex. By supplementing a deficient diet with chemically pure vitamins Fraenkel and Blewett have shown that the vitamin requirements vary considerably from insect to insect (*Biochem. J.*, 1943, **37**, 686). The beetles *Ptinus* and *Tribolium* require at least six of the B vitamins for adequate growth. On the other hand, the requirements of the Anobiid beetles *Lasioderma* and *Sitodrepa* are quite different: the growth of the first is slightly benefited by the addition of four B vitamins, while the second requires the addition of thiamin only. These differences can be attributed to the presence of intracellular symbionts in *Lasioderma* and *Sitodrepa* and their absence in the other insects. The symbionts can be shown to be supplying B vitamins if the larvæ are freed from symbionts by sterilising the eggs. Sterile larvæ of both species fail to grow in the absence of at least five vitamins of the B-group (*Proc. Roy. Soc. B.*, 1944, **132**, 212).

Many years ago the suggestion was made that the symbiotic micro-organisms which occur in all blood-sucking insects supply their host with some necessary food substance that is lacking in blood. The growth of the Triatomid bug *Rhodnius* in the absence of its symbionts has recently been investigated by G. Brecher and V. B. Wigglesworth (*Parasitology*, 1944, **35**, 220). The organism, *Actinomyces rhodnii*, invariably occurs in the gut of the bug. It is not transmitted through the egg, but is taken up by the young nymph from the contaminated egg-shell or from the excreta of other bugs. Insects reared from sterilised eggs grow and moult normally until the 4th or 5th instar, when moulting becomes delayed. Few insects become adult and these are incapable of reproduction. There is evidence that the *Actinomyces* provides a vitamin of the

B-group; this in turn may be needed for the production of the moulting hormone.

Other micro-organisms may play a more direct rôle in the nutrition of the host insect. Hemiptera feeding on plant sap acquire only a small proportion of protein in their diet; some, for example aphids, ingest very large quantities of sap but whether the protein thus acquired by these insects suffices to meet the demands made by their enormous reproductive capacity has been questioned. According to L. Tóth, A. Wolsky and M. Bátori (*Z. vergl. Physiol.*, 1942, **30**, 67), the mycetomes of aphids and of the Cercopid *Aphrophora* harbour bacteria, possibly *Azotobacter*, capable of the fixation of atmospheric nitrogen. Following the technique adopted for root nodule bacteria these authors cultured macerated insect tissues in dilute oxaloacetic acid. Micro-kjeldahl estimations showed that the nitrogen content of the medium was often considerably enriched, sometimes by as much as 100 per cent., after incubation for five hours at 25° C.

GENETIC STRUCTURE OF *DROSOPHILA* POPULATIONS AND SPECIATION.—Since the discovery of the common occurrence of recessive mutations in natural populations of *Drosophila*, further work has continued to emphasise the extent of the concealed genetic variability. T. Dobzhansky, A. M. Holz and B. Spassky (*Genetics*, 1942, **27**, 463) have studied this variability in natural populations of *D. pseudoobscura*. When homozygous, 21 per cent. of the second and 41 per cent. of the fourth chromosomes recovered from wild flies were found to reduce the viability of the stock, while 1 per cent. and 0·5 per cent. improved the viability. Similarly, a high proportion of the chromosomes carried genes reducing the rate of development, many fewer hastening it. A significant proportion also carried sterility genes, and a smaller number visible mutants. The authors point out that it is the adaptive level of the heterozygotes rather than the accumulation of deleterious recessive genes that is of greater significance. Only in very small breeding populations will the viability of the homozygotes assume much importance. *D. pseudoobscura* is a species breeding in moderately small units in arid mountain regions. In the much larger breeding populations of American *D. melanogaster* deleterious (lethal or semi-lethal) mutants are carried by as many as 67 per cent. of the second chromosomes (P. T. Ives, *Genetics*, 1945, **30**, 167). These populations appear to be largely maintained by heterosis. The species would conceivably suffer if forced into smaller breeding units.

A genotype which is unfavourable under one set of environmental conditions may be neutral or favourable under others.

T. Dobzhansky and B. Spassky (*Genetics*, 1944, **29**, 270) have compared the behaviour of flies homozygous or heterozygous for 26 second and 22 fourth wild chromosomes when temperatures, population densities and culture conditions were varied. A great deal of potential adaptive variability was uncovered. For example one genotype was normal at 16° C., but completely lethal to flies reared at 25° C. Some genotypes were more favourable at nigh, others at intermediate or high population densities. Some viabilities superior to normal (wild type) flies were observed, but none was superior under all conditions. The rate of development is a more stable character and homozygotes showing a slowed development in one environment were also slower in others.

The full extent of the plasticity in the genetic structure of natural populations has only recently been realised. T. Dobzhansky (*Genetics*, 1943, **28**, 162) has taken samples of *D. pseudoobscura* from three localities throughout the year and has followed the relative frequencies of certain gene arrangements in the third and X chromosome by salivary gland analysis. These frequencies were found to change from month to month; moreover, they were regular and cyclic, following the annual climatic cycle. The changes are believed to be caused by natural selection favouring the carriers at certain seasons, for they can be partially reproduced when fly populations are kept in cages under controlled temperature conditions (T. Dobzhansky and S. Wright, *Genetics*, 1946, **31**, 125). The selective value is probably due to their association with genes conferring physiological advantages rather than to the arrangements themselves.

Only a few years ago it appeared as if *Drosophila* were not a very favourable organism for studying the mechanisms of evolution; the unique weapon of salivary gland analysis could be applied only to the few cases of interspecific hybridization then reported. Now at least sixty cases of hybridization between species or subspecies have been described. Advances in taxonomy (A. H. Sturtevant, *Univ. Texas Publ.*, No. 4213, 1942) and in our knowledge of the distribution of the Drosophilidæ (*e.g.* J. T. Patterson *et al.*, *Univ. Texas Publ.*, Nos. 4313 and 4455) have proceeded alongside these genetic studies.

It is becoming apparent that speciation in *Drosophila* is commonly associated with the accumulation of gene differences rather than with the occurrence of large sectional chromosome rearrangements, although these may arise after effective isolation has been established. Of particular interest is the circumstance that the various isolating mechanisms, of which the commonest are geo-

graphical or ecological isolation, sexual incompatibility and hybrid sterility, appear to be operating independently and to a variable extent in different groups of species and subspecies. Morphological differences have no constant significance. Some groups in which the physiological and genetic barriers to interbreeding are fully established are indistinguishable, while other geographical strains are separable by many morphological differences but are not as yet isolated as breeding units. The following examples are taken mainly from the extensive work of J. T. Patterson and his associates (*Univ. Texas Publ.*, No. 4228 (1942), and No. 4455 (1944)).

Geographical strains of the species *D. repleta* differ by a whole ensemble of genes and show considerable sexual isolation. When induced to breed together, however, no consistent cross-sterility is observed (L. T. Wharton, 1942). Sexual isolation in this case may function to establish within the large population smaller units whose flexibility favours rapid evolutionary changes.

The *funebris* group includes the cosmopolital species *D. funebris* and the indigenous North American species *D. subfunebris* and *D. macrospina*. The latter has become differentiated into at least three subspecies, namely *macrospina*, *ohioensis* and *limpiensis* (G. B. Mainland, 1942). In crosses between the last three there is a variable degree of hybrid sterility, but its extent is less when strains of decreasing geographical separation are crossed. This is entirely different from the well-known case of *D. pseudoobscura* and *D. miranda* investigated by Dobzhansky, where strains of *pseudoobscura* from "*miranda*" localities are more effectively isolated from interbreeding with *miranda* than are strains from localities where *miranda* is absent. The probable explanation is that the distribution of *pseudoobscura* and *miranda* is overlapping, and selection favours the evolution of mating barriers between populations of flies adapted to a particular set of environmental conditions. The *macrospina* subspecies, on the other hand, replace one another across the continent, and being wood-dwelling forms are probably breeding in comparative isolation from one another.

A somewhat similar case of incipient isolation is described in *D. pallidipennis* by J. T. Patterson and T. Dobzhansky (*Genetics*, 1945, **30**, 429). The two subspecies *pallidipennis* and *centralis* occur in Brazil and Mexico respectively. Fresh specimens can just be distinguished morphologically. Their gene arrangements are identical save for one autosomal inversion. In other respects the situation is almost the reverse of the *repleta* example, for, whereas no sexual isolation exists between the two subspecies, the male hybrids are completely sterile.

Differentiation is further advanced in the species *D. mulleri* and *D. aldrichi*. In southern Texas where their distribution is largely overlapping, these species are associated with *Opuntia*, the larvæ feeding on certain strains of yeasts in the rotting fruits (R. P. Wagner, 1944). Sexual isolation is not complete, however, for a few sterile male hybrids are found in nature (J. F. Crow, 1942). In this case *mulleri* and *aldrichi* may have developed incompatibility through the accumulation of gene mutations while in isolation and once present this has permitted the two species to colonise the same habitat.

In view of the prevalence of sexual isolating mechanisms in *Drosophila* it is interesting to find that they may arise quite readily, sometimes as the result of a single gene mutation. A case has recently been described in *D. obscura* by J. M. Rendel (*J. Genet.*, 1945, **46**, 287). The flies have a very definite mating behaviour which depends upon vision. The male courts the females by flicking and spreading his wings or by sticking out his proboscis, thus fixing her attention before he attempts to copulate. The female may refuse the attentions of the male by walking or flying away, twisting her abdomen or kicking with the middle legs. The latter sign is always taken by the male as a final refusal. Male flies homozygous for yellow appear to be distasteful to wild type females, and are nearly always refused by them in this manner. Yet the courtship of yellow females by yellow males is completely successful.

The Bionomics and Control of the Carrot Fly in England.—In East Anglia the carrot fly *Psila rosæ* passes through two and sometimes a partial third generation (D. W. Wright and D. G. Ashby, *Ann. appl. Biol.*, 1946, **33**, 263). The first generation flies emerge in May and lay their eggs in the soil near the carrot plant. The larvæ give rise to the second generation of flies which emerge from August to October. The overwintering population in the soil consists of eggs, larvæ and pupæ.

Heavy damage by the mining of the larvæ may result in unmarketability and total loss of the crop. Now in most fields the heaviest maggot damage occurs round the edges and headlands (F. R. Petherbridge, D. W. Wright and D. G. Ashby, *Ann. appl. Biol.*, 1942, **29**, 380). This distribution has been traced to the behaviour of the adult. The insects are weak flyers and after emergence assemble in the hedgerows for shelter (F. T. Baker *et al.*, *Ann. appl. Biol.*, 1942, **29**, 115; F. R. Petherbridge and D. W. Wright, *ibid.*, 1943, **30**, 348). The dispersal of the flies from shelter is greatly influenced by the meteorological conditions. When the wind is not too strong, particularly on warm sunny days, the flies

leave the hedgerows in the late afternoon, moving into the fields to oviposit. Afterwards they drift downwind and take shelter again. Previous cultural practices included the late sowing of carrots to avoid the first generation of flies. The fuller understanding of the biology of the pest has enabled further recommendations to be made and has rendered control practicable. The measures proposed include the sowing of carrots in large fields, trimming hedges, keeping ditches free from weeds and eliminating shelter in the form of neighbouring crops such as potatoes. The ideal means of control appears to be the complete coverage of the headland vegetation with a residual deposit of a lasting insecticide such as DDT (F. R. Petherbridge *et al.*, *Ann. appl. Biol.*, 1945, **32**, 262). Suitably applied round the edges of the field the insecticide affords complete protection from carrot fly for as long as three weeks.

NOTES

Technetium and Astatine (F. P. D.)

In letters to *Nature* of January 4, 1947, proposals are made for naming the two elements of atomic numbers 43 and 85.

C. Perrier and E. Segrè in 1937 and 1938 showed that radioactive isotopes of element 43 could be formed by neutron or deuteron bombardment of molybdenum by the 37-in. cyclotron at the University of California. Several chemical properties of the element were established at the same time. In 1940 C. S. Wu and E. Segrè found element 43 among the fission products of uranium, a source from which relatively large amounts of the element can be isolated. The name "technetium," derived from the Greek τεχνητός, artificial, is proposed for the element, since this is the first element to be made artificially. The chemical symbol is Tc.

D. R. Corson, K. R. Mackenzie and E. Segrè in 1940 prepared an isotope of mass 211 of element 85 by bombarding bismuth with alpha particles in the 60-in. cyclotron at the University of California. Several chemical properties of element 85 were established and a complete nuclear study of the isotope formed was made. Since this is the only halogen without stable isotopes, it is proposed to name it "astatine" from the Greek ἄστατος, unstable. The chemical symbol is At.

Miscellanea

A long New Year Honours List contained the names of the following scientists and others associated with scientific work: *O.M.*: Field Marshal J. C. Smuts. *K.C.V.O.*: Mr. Evelyn C. Shaw, secretary to the Commissioners of the Exhibition of 1851. *Knights:* Major-General H. C. Buckley, formerly principal of the Medical College, Agra; Dr. W. H. Coates, a deputy-chairman of Imperial Chemical Industries, Ltd.; Prof. Kerr Grant, professor of physics in the University of Adelaide; Prof. W. N. Haworth, Mason professor of chemistry in the University of Birmingham; Prof. C. E. Hercus, professor of bacteriology and preventive medicine in the University of Otago; Dr. E. W. Smith, lately president of the Institute of Fuel; Mr. R. Thomas, agricultural adviser to the Government of Sind. *C.B.*: Air Commodore F. Whittle. *C.M.G.*:

Prof. P. A. Buxton, professor of entomology in the University of London, London School of Hygiene and Tropical Medicine; *C.I.E.:* Mr. A. P. F. Hamilton, inspector-general of forests, India; Colonel O. Slater, director of the survey of India; Lieut.-Colonel W. J. Webster, senior assistant director, Central Research Institute, Kasauli. *C.B.E.:* Prof. F. T. Brooks, professor of botany in the University of Cambridge; Mr. O. V. Guy, secretary of the Cambridge University Appointments Board; Prof. T. D. Jones, professor of mining in the University of Wales, University College, Cardiff; Dr. F. C. Toy, director of the British Cotton Industry Research Association; Prof. T. Wallace, director of the Bristol University Agricultural and Horticultural Research Station, Long Ashton.

At the anniversary meeting of the Royal Society, held on November 30, the Royal Medals of the Society for 1946 were presented to Sir Lawrence Bragg, Cavendish professor of experimental physics in the University of Cambridge, for his distinguished researches on the structure of solids, and to Dr. C. D. Darlington, director of the John Innes Horticultural Institution, in recognition of his distinguished contributions to cytology. The following medals were also awarded: The Copley Medal to Prof. E. D. Adrian, professor of physiology in the University of Cambridge, for his outstanding contributions to nerve physiology. The Rumford Medal to Sir Alfred Egerton, professor of chemical engineering in the University of London, Imperial College of Science and Technology, for his distinguished researches on combustion. The Davy Medal to Prof. C. K. Ingold, professor of chemistry in the University of London, University College, for his outstanding researches in physico-organic chemistry. The Darwin Medal to Sir D'Arcy Wentworth Thompson, professor of natural history in the University of St. Andrews, in recognition of his distinction as a zoologist. The Sylvester Medal to Prof. G. N. Watson, professor of pure mathematics in the University of Birmingham, for his distinguished contributions to mathematical analysis. The Hughes Medal to Prof. J. T. Randall, Wheatstone professor of physics in the University of London, King's College, for his distinguished contributions to applied physics, and especially the development of the magnetron.

The following have been elected officers of the Society: Sir Robert Robinson, president; Sir Thomas Merton, treasurer; Sir Alfred Egerton and Sir Edward Salisbury, secretaries; Prof. E. D. Adrian, foreign secretary.

Dr. C. J. Mackenzie, president of the National Research Council of Canada, has been elected a Fellow of the Royal Society under

the statute which provides for the election of persons who either have rendered conspicuous service to the cause of science or are such that their election would be of signal benefit to the Society.

The Nobel Prize for Physiology and Medicine for 1946 has been awarded to Dr. H. J. Muller, and the Prize for Physics to Prof. P. W. Bridgman. The Prize for Chemistry is shared by Prof. J. B. Sumner, professor of biochemistry in Cornell University, and jointly by Dr. W. M. Stanley and Dr. J. H. Northrop of the Rockefeller Institute for Medical Research, Princeton, N.J.

The Dr. W. S. Bruce Memorial Prize for 1946 has been awarded by the Joint Committee of the Royal Physical Society of Edinburgh, the Royal Scottish Geographical Society and the Royal Society of Edinburgh to Lieut-Colonel P. D. Baird for his valuable survey and geological work with Mr. J. M. Wordie in North-West Greenland and Baffin Island in 1934, and with Mr. T. H. Manning's British Canadian Arctic Expedition in 1936–37.

The Cambridge Philosophical Society have awarded the Hopkins Prize for the period 1933–39 to Prof. J. D. Cockcroft, director of the Atomic Energy Research and Development Establishment at Harwell, for researches on the artificial transmutation of elements; and to Prof. E. A. Milne, Rouse Ball professor of mathematics in the University of Oxford, for researches on stellar structure and cosmology.

The Gold Medal for 1947 of the Royal Astronomical Society has been awarded to Prof. M. G. J. Minnaert, of Utrecht, for his outstanding contributions to solar physics, particularly solar spectrophotometry.

Dr. Karl Weissenberg of the Shirley Institute, Didsbury, Manchester, has been awarded the Duddell Medal of the Physical Society, in recognition of his invention and development of X-ray goniometers.

Other medals awarded include those of the Geological Society of London: the Wollaston Medal to Dr. J. B. Tyrrell, the Murchison Medal to Mr. Percy Evans, the Lyell Medal to Dr. Stanley Smith, and the Bigsby Medal to Dr. G. H. Mitchell; the Symons Medal of the Royal Meteorological Society to Prof. D. Brunt; the Faraday Medal of the Institution of Electrical Engineers to Sir Leonard Pearce; the Baker Medal of the Institution of Civil Engineers to Mr. G. L. Groves; the Cadman Medal of the Institute of Petroleum to Mr. R. P. Russell; the Hinchley Medal of the British Association of Chemists to Mr. C. S. Garland.

Sir Henry Tizard, K.C.B., F.R.S., has been appointed chairman

of the new Defence Research Policy Committee and of the Advisory Council on Scientific Policy.

Sir Ben Lockspeiser, director-general of scientific research (air) at the Ministry of Supply, has been appointed chief scientist to the Ministry.

The National Coal Board have appointed Dr. W. Idris Jones to be director-general of research, and Prof. H. L. Riley of the University of Durham to be director of carbonisation research.

Prof. A. V. Hill, Foulerton research professor of the Royal Society, has been elected a trustee of the British Museum.

Dr. Julian Huxley, executive secretary of the Preparatory Commission of UNESCO has been appointed director-general of the Organisation.

Dr. R. A. Silow, until recently scientific officer of the Agricultural Research Council at the Plant Breeding Institute, Cambridge, has been appointed director of the British Council's Science Office in China, in succession to Dr. Joseph Needham.

Mr. G. V. B. Herford has been appointed director of the Pest Infestation Laboratory of the D.S.I.R. at Slough.

Dr. T. W. J. Taylor, C.B.E., is principal-designate of the new University College of the West Indies, to be established in Jamaica.

The following University appointments have been announced: Prof. G. C. Allen, professor of political economy in the University of London, University College; Mr. A. J. Ayer, Grote professor of philosophy of mind and logic in the University of London, University College; Dr. N. A. Burges, professor of botany in the University of Sydney; Mr. W. L. S. Fleming, director of the Scott Polar Research Institute, University of Cambridge; Dr. H. Jeffreys, Plumian professor of astronomy and experimental philosophy in the University of Cambridge; Dr. F. Coles Phillips, George Herdman professor of geology in the University of Liverpool; Dr. F. J. W. Roughton, John Humphrey Plummer professor of colloid science in the University of Cambridge; Prof. P. C. Sarbadhikary, Sir Rash Behari Ghosh professor of botany in the University of Calcutta; Dr. R. J. Sarjant, professor of fuel technology in the University of Sheffield; Mr. N. J. Scorgie, Courtauld professor of animal husbandry, veterinary hygiene and dietetics at the Royal Veterinary College; Dr. E. A. Stewardson, professor of physics at University College, Leicester; Dr. S. Tolansky, professor of physics in the University of London, Royal Holloway College; Dr. C. H. Waddington, professor of animal genetics in the University of Edinburgh; Dr. W. L. Waterhouse, research professor in agriculture in the

University of Sydney; Dr. A. G. Walker, professor of mathematics in the University of Sheffield.

We have noted with great regret the announcements of the death of the following scientific workers: Mr. W. Barnicot, M.B.E., secretary of Rothamsted Experimental Station; Prof. J. Shaw Bolton, emeritus professor of mental diseases, University of Leeds; Prof. R. M. Ferrier, emeritus professor of civil engineering, University of Bristol; Sir John Flett, K.B.E., F.R.S., formerly director of the Geological Survey of Great Britain and the Museum of Practical Geology; Prof. T. W. Griffith, C.M.G., emeritus professor of medicine in the University of Leeds; Mr. A. B. Jackson, botanist; Prof. W. L. Jepson, emeritus professor of botany in the University of California; Prof. J. G. Koenigsberger, professor of physics in the University of Freiburg; Prof. P. Langevin, For.Mem.R.S., director of the École de Physique et Chimie Industrielle, Paris; Prof. H. P. Lewis, professor of geology in the University College of Wales, Aberystwyth; Dr. A. Liebert, sometime director of the Kant-Gesellschaft and extra-ordinary professor of philosophy in the University of Berlin; Dr. Dorothy Jordan Lloyd, director of the British Leather Manufacturers' Research Association; Mr. J. K. Lubanski, physicist; Dr. C. T. Madigan, lecturer in geology in the University of Adelaide; Prof. K. Mannheim, professor of education in the University of London; Prof. E. L. Mark, emeritus professor of zoology in Harvard University; Dr. H. Obermaier, prehistorian; Dr. H. Roberts, writer on social medicine and related topics; Mr. W. H. Roberts, recently city analyst of Liverpool and associate professor of public health chemistry in the University of Liverpool; Mr. C. C. Robertson, formerly chief research officer and professional assistant to the chief conservator of forests, Department of Forestry, South Africa; Mr. C. Rodgers, O.B.E., deputy director of the British Electrical and Allied Manufacturers' Association; Prof. F. M. Rowe, F.R.S., professor of colour chemistry and dyeing in the University of Leeds; Mr. J. W. Sandström, formerly director of the Stockholm Meteorological and Hydrographic Institute; Prof. A. E. Tchitchibabin, chemist; Mr. R. N. Vyvyan, formerly engineer-in-chief of the Marconi Co.; Mr. J. D. Watson, formerly engineer to the Birmingham, Tame and Rea Drainage Board; Brigadier H. St. J. L. Winterbotham, C.B., C.M.G., D.S.O., formerly director-general of the Ordnance Survey.

The Society of Dyers and Colourists inform us that Mr. J. Barritt, Head of the Department of Chemical Technology at the Wool

Industries Research Association, has been appointed Hon. Secretary in succession to the late Mr. J. S. Ridsdale, and that Mr. C. L. Bird, lecturer in dyeing at Leeds University, has been appointed Editor of the Journal of the Society in succession to the late Prof. F. M. Rowe.

We are asked to draw attention to the meetings of the West Middlesex and South Buckinghamshire Scientific Society, which are held once a month at Bishopshalt School, Hillingdon. One paper, lasting 60 to 90 minutes, is read at each meeting, followed by a discussion. Field and joint meetings are held in the summer months. The Hon. Secretary is Mr. C. J. S. Bromfield, "Dingle Combe," Potters Cross, Iver Heath, Bucks.

The *Bulletin of the Imperial Institute* (Vol. XLIV, No. 3, July–September 1946) contains an account of the search for oil carried out in England and Scotland since the last report on the work was issued in 1939. The results of very extensive drilling have, on the whole, been disappointing. Six oilfields have been found : four in Nottinghamshire, one in Lancashire and one in the Midlothian area of Scotland. Up to June 1946 the Midlothian field had yielded about 2000 tons of oil, the field in the Formby area of Lancashire 6900 tons and only the wells in the Nottingham area had produced any really useful quantity of oil. Here 237 wells have yielded over 430,000 tons—an output comparable with that of an average field in the Mid-Continent area of the U.S.A. The wells at Eakring are most productive and have given about three-quarters of the total output : a test well at Duke's Wood was drilled to 7476 ft., the greatest depth yet reached in Great Britain. The wells, now operated by pumping, give a greenish-brown oil of a paraffinic nature. The motor and aviation spirit distillates have a high octane value ; high-grade lubricating oils can be prepared.

Since the end of the War the D'Arcy Exploration Co. and the Anglo-American Oil Co. have taken out licences for drilling over an area of about 16,000 sq. miles. Much drilling has been done but no useful results have been reported. The present rate of production is 4500 tons per month ; in September 1943 a peak rate of 10,000 tons was attained.

The same issue of the *Bulletin* contains a detailed account of the geology of the Namwele-Mkomolo coalfield which lies between Lake Rukwa and the southern end of Lake Tanganyika. The Namwele area has coal reserves above the 2000-ft. level estimated at 4 million tons and there is possibly rather more than half as much in Mkomolo.

The coal is a high volatile bituminous coal with a high ash (> 25 per cent.) and sulphur (*c.* 7 per cent.) content.

We have received copies of several issues of the monthly *Bulletin of the British Scientific Instrument Research Association*, which first appeared in April, 1946. Intended primarily for the use of members of the Association it is supplied to non-members at a cost of £2 per year. The offices of the Association are at 26 Russell Sq., London, W.C.1, and here also are the Information Department and the Library. The laboratories have just been transferred to "Sira," Southill, Elmstead Woods, Chislehurst, Kent, where there is ample space for experimental work and excellent equipment including, for example, glass-making crucible furnaces, high vacuum plant and an electrical sub-station capable of supplying a maximum demand of 100 kVA. The *Bulletin* contains a page or so devoted to Association notes and rather less than 20 pages containing a survey of current literature relating to scientific instruments, lists of additions to the library and of reports on German industry: in all a most useful publication.

The issues of the *Bell Laboratories Record* for October, November and December 1946, contain descriptions of many more appliances devised or developed in the Laboratories during the war and of a few developed since its conclusion. Examples of the former are the SL Radar System used by naval surface craft, the SJ System used by submarines when surfaced at night, and the non-linear coils used as pulse generators for magnetrons. There are also details of the arrangements for the use of Western Electric Fastax cameras at Bikini with three very clear photographs of the water column and smoke cloud produced by the explosion. Peace-time developments include a teletypewriter and converter control unit for use with radio telephone systems on aeroplanes. There is also a description of an experimental model of a new and very unusual type of valve—"the beam travelling-wave tube"—used to amplify microwave frequency signals and capable of transmitting a broad band of frequencies—*e.g.* 800 megacycles—without diminution of the gain factor. The weak input signals are fed through a wave guide on to an antenna connected to one end of a long wire helix in an evacuated tube and are delivered by another antenna at the other end of the helix to an output wave guide. A stream of electrons, produced by the usual form of electron gun, passes through the centre of the helix with a speed a little greater than that of the wave and the amplification is produced by the interaction of the electric field of the helix with

these electrons. It is stated that the possibility of this mode of amplification was first shown during the war by workers in the Clarendon Laboratory, Oxford.

The Chemical Society is to celebrate from July 14 to July 17 next the centenary of its foundation. But for the war the celebrations would have taken place in 1941. It was the first society formed solely for the study of chemistry; although there had been small private chemical societies before 1841, none lasted for any great length of time. At the first general meeting Thomas Graham, one of the most distinguished chemists of his time and the pioneer of colloid chemistry, was elected the first President. The present President is Professor C. N. Hinshelwood, M.A., Sc.D., F.R.S., who will deliver the centenary address at the Central Hall, Westminster, on Tuesday, July 15. The Faraday Lecture will be given by Sir Robert Robinson, M.A., D.Sc., LL.D., P.R.S., on the following day.

Dr. J. P. Lawrie, Editor of *Chemical Products and the Chemical News*, has written a booklet entitled *Chemicals from Methane* (Science Services, Ltd., price 3*s*.). He stresses the amount of waste in this country and says that "the utilization of natural gas constitutes a challenge to applied science and the economy of the nation." Line diagrams are given of the carbon black plant, the conversion process for hydrogen and for acetylene manufacture, which incidentally could have been improved by adequate lettering. Nevertheless, the booklet is well worth studying in view of the paramount necessity for the maximum use of all raw materials available in this country.

After an interval of seven years, brought about by the German occupation of the country, the *Collection of Czechoslovak Chemical Communications* is again appearing monthly. The subscription is 400 crowns (or £2). The journal will publish articles on all branches of pure chemistry.

ESSAY REVIEWS

BINOCULAR COLOUR MATCHING: A NEW TECHNIQUE. By W. S. Stiles, D.Sc., Principal Scientific Officer, The National Physical Laboratory. Being a Review of **Researches on Normal and Defective Colour Vision.** By W. D. Wright, A.R.C.Sc., D.Sc., Reader in Colour Vision, Imperial College of Science and Technology, London. [Pp. xvi + 383, with 233 figures.] (London: Henry Kimpton, 1946. 36*s*. net.)

It is thirty-three years since Sir William Abney published his *Researches on Colour Vision*, and the book before us with a very similar title comes from another worker at the Imperial College. Dr. Wright, like his predecessor, approaches his subject as a physicist. He is concerned with determining the light stimuli which, when presented to a normal or colour-defective eye under carefully controlled conditions, produce identical sensations of colour and brightness, or just perceptibly different sensations, or sensations of equal brightness but different colour and so on. The researches which he and his co-workers have carried out over the last twenty years, and which form the main content of this book, have not dealt directly with the histology, biochemistry or electrophysiology of the retina, nor with those aspects of visual perception in which the activity of the higher nervous centres is clearly manifest. It may be noted with satisfaction, therefore, that the author has shown a proper regard for the results of these other methods of attack when discussing his own work. The latter began in 1926 with a re-determination of the trichromatic coefficients of the spectrum colours, and for this a new colorimeter employing monochromatic matching stimuli was designed. The measured coefficients for ten normal observers were subsequently combined with similar results obtained at the National Physical Laboratory by Mr. Guild to provide the quantitative definition of a standard colorimetric observer which was adopted internationally in 1931 and is now fully established in colour technology. The new colorimeter proved an adaptable instrument of research and with its aid Dr. Wright and other workers at the Imperial College made extensive determinations of the colour coefficients and luminosity curves of colour defective observers—dichromats and anomalous trichromats—and of the powers of colour discrimination of both normals and colour-

defectives. A new phase began in 1934 with the development of binocular colour-matching, in which a test colour viewed by the right eye is matched with a mixture of three primary stimuli viewed with the left eye. The modifications of the binocular match are determined which follow the exposure of the right eye to different preliminary adapting lights, white or coloured, the left eye being kept in a standard dark-adapted condition. In this way, Dr. Wright brought within the scope of measurement a large group of phenomena concerned with colour adaptation. More recently, attention has been turned to the appreciation of luminosity and colour in slightly indirect as compared with direct vision and to the loss of colour discrimination in very small matching fields.

Excepting the measurements by binocular colour-matching, much of this work is not new in principle. But no comparable accumulation of reliable quantitative data on the colour properties of normals and defectives has been available hitherto. For this reason, if for no other, Dr. Wright's book will be of great value to those concerned with colour technology or with the detection and assessment of colour defects. Of particular importance for the research worker, on the other hand, is the fairly detailed account of the investigations on colour adaptation which include some previously unpublished measurements for the case when only the parafoveal retina is exposed to the adapting stimulus. To illustrate the kind of result being obtained in this field, we may consider very briefly the progress made on one of the key problems of colour vision, the determination of the spectral sensitivity curves of the trichromatic mechanisms.

Monocular colour-matching provides an infinity of possible sets of three spectral sensitivity curves, but only one of these can represent the properties of the actual physiological mechanisms. Dr. Wright argued that a test stimulus of such a character that it stimulated one mechanism only, would appear of the same colour, although not necessarily of the same brightness, whatever the previous stimulation of the eye by white or coloured adapting fields. No actual test stimuli satisfied this condition completely but from the observed colour changes, measured by the binocular method, for suitably selected test stimuli and adapting fields, it was possible to determine by calculation three hypothetical stimuli possessing the desired property. As usual, by "hypothetical stimuli" is meant here stimuli whose trichromatic specifications in terms of any real primary lights must involve negative coefficients. Once these fundamental stimuli were known the corresponding spectral sensitivity curves could be calculated from the data of

monocular colour-matching. The first application of this method gave curves with maxima located respectively at 440, 540, 580 mμ (approx.), in general agreement, in this respect, with the curves proposed by König from a consideration of the properties of colour-blinds.

The derivation of the fundamental stimuli in this way assumed that the additivity laws of colour matching would also apply in the binocular method. Thus it assumed that if, at a given time after extinguishing the adapting field, a stimulus A in the light-adapted right eye matched a stimulus a in the dark-adapted left eye, and also a stimulus B, right eye, matched a stimulus b, left eye, then the mixed stimulus $\overline{A + B}$, right eye, would match the mixed stimulus $\overline{a + b}$, left eye. This assumption was found to hold approximately for the conditions of the first determination of the fundamental stimuli. Further measurements showed, however, that it was not true in general. Some deviations might be expected if for one or more of the trichromatic mechanisms the relation between response and intensity of the stimulus was different in the light-adapted right and the dark-adapted left eye. But the observed deviations appeared too radical to be explained on these lines. For example, in some cases, the response of a particular mechanism to test stimulus A was actually reduced by adding the test stimulus B.

This breakdown of the so-called *coefficient law* (v. Kries) is one of the pieces of evidence—there are several others provided by the binocular measurements—which lead to the conclusion that the notion of three *independent* colour mechanisms is inadequate. All the anomalies relate to the eye in a state of change after the abrupt removal of an adapting stimulus. Could they be attributed to after-images of the adapting stimulus? The answer is no, the measurements are inconsistent with this view if by after-image is meant a luminosity such as would be produced by a veil of light superimposed on the test stimulus, the intensity and colour-quality of the veil being dependent only on the adapting stimulus. In looking for an explanation of these results Dr. Wright introduces two ideas: (*a*) complex after-images of the adapting stimulus which are modified by or even elicited by the test stimulus, (*b*) interaction between the three mechanisms during the recovery process, causing the response of one mechanism to the test stimulus to be intensified or inhibited by the responses of the others. These ideas are formulated only in very general terms and hardly amount at present to a new working hypothesis to replace the simple form of trichromatic theory. It is very much to be hoped that work on this promising line will be continued both in Dr. Wright's laboratory and elsewhere.

Binocular colour-matching is a new technique not yet fully exploited. Measurements of least perceptible colour differences on the other hand have been used, since the time of Helmholtz, in making deductions about the colour mechanisms. Nevertheless, their interpretation is still controversial. The discussion of this question is the least satisfactory feature of the present book. Dr. Wright is anxious to avoid over-simplified theories, such as the assumption that a just perceptible difference of intensity corresponds at all intensity levels to the same difference of photochemical decomposition in the retina. He works instead with a general analysis on the following lines. A stimulus depending on a physical variable J produces a sensation specified by the quantity Q. The observed least perceptible difference ΔJ is determined by the rate of change of sensation with stimulus $\frac{dQ}{dJ}$ (the physiological factor), and by the smallest difference of sensation ΔQ appreciable under the prevailing conditions of observation (the psychological factor). Thus, he puts $\Delta J = \Delta Q \Big/ \left(\frac{dQ}{dJ}\right)$. The intention behind this splitting-up of the process occurring in discrimination experiments is no doubt to emphasise the operation of both peripheral and central factors. But it seems a pity that Dr. Wright should choose to develop his ideas in terms of the very controversial notion of sensation magnitude. He himself observes:

"We have no means, other than by the very unreliable method of mental introspection, of obtaining quantitative information about the magnitude of our sensations and without such data we can hardly hope to derive a formal relation between stimulus and sensation."

Other workers in this field would go further and would regard expressions such as 'the magnitude of the sensation of hue' as meaningless. The use of quantitative sensation as though it were a well-defined concept leads inevitably to obscurities. Thus on p. 191 in discussing hue discrimination it is implied that earlier theories determined $\frac{dQ}{dJ}$ from the slopes of the spectral sensitivity curves of the three receptor processes and went wrong in assuming ΔQ to be constant through the spectrum. But if the author admits that in these theories $\frac{dQ}{dJ}$ was in fact determined, his statement quoted above is contradicted. On the other hand, if $\frac{dQ}{dJ}$ was not

determined, the criticism of these theories can hardly apply in the form stated. Again, it is suggested (p. 194) that uncontrollable variations in the magnitude of the sensation from different parts of a uniform stimulus field may explain the finite size of the least perceptible differences of intensity, wave-length, etc., between two such uniform fields seen juxtaposed. This theory rests on a rather dubious analogy which certainly seems to depend on the notion of sensation. But in the subsequent development "sensation" is quietly replaced by "response," and a final comment suggests that the theory shows "a reasonable explanation of brightness discrimination data can be given without any reference to sensation magnitudes whatsoever." All this is a very minor criticism of an excellent book. Among the things particularly well done may be mentioned the clear explanation of the limited inferences which can be drawn from the convergence or parallelism in the trichromatic chart of the iso-colour zones of dichromats, and the discussion of macular pigmentation. With regard to the latter, the author is careful to point out that we are not yet in the position to disentangle completely the effects of a pigment layer and of variations in the relative sensitivities of the underlying trichromatic mechanisms.

It can be predicted with confidence that Dr. Wright's book will have an honoured place on the bookshelves of research workers on vision for many years to come.

A NEW ORGANIC CHEMICAL NOTATION. By A. R. Todd, M.A., D.Sc., F.R.S., Professor of Organic Chemistry in the University of Cambridge. Being a Review of **A New Notation and Enumeration System for Organic Compounds.** By G. Malcolm Dyson, M.A., Ph.D., F.R.I.C. [Pp. iv + 63.] (London, New York, Toronto: Longmans, Green & Co., 1947. 7*s.* 6*d.* net.)

Organic chemistry, one of the most intricate and highly systematised branches of science, is undoubtedly rendered more difficult for the student and the professional chemist alike by its deficiencies in nomenclature. Moreover, the enormous expansion of the subject which has occurred in the past twenty years has not only revealed the inadequacy of existing systems of nomenclature but has led to their piecemeal and random modification to such an extent that they have virtually broken down, and in so doing have created such chaos in the literature that further progress is hampered by the difficulty of systematising, or even reviewing, existing knowledge. It is no accident that Beilstein's famous *Handbuch der Organischen Chemie*, the major reference work in the subject, covers the literature only up to 1930 in its latest supplements and that the

possibility of its being brought up-to-date under the existing system appears to be remote. It is to this great problem of systematic nomenclature and unequivocal notation of organic compounds that Dr. Dyson has addressed himself in the monograph under review.

The deficiencies of the systematic organic chemical nomenclature proposed by international agreement at Geneva in 1892, and modified by the Liège report of 1930, are well known. A large number of compounds have under this system names so unwieldy and unpronounceable that they are of little value, while others lie completely outside its scope. Efforts to circumvent these difficulties have led to the use of trivial names in great variety, and this, coupled with differences in enumeration of ring systems in British, American and Continental chemical journals, has led to a situation in which a literature search for information on any individual compound is a laborious operation which is not always successful and which is a constant source of delay and irritation to all chemists. In the early portion of his book, Dr. Dyson discusses these various difficulties, illustrating them with examples taken from the chemical literature, and his case that this situation cannot be remedied by anything save a revolutionary change in our system of notation is unanswerable; each attempt in the past to put matters right by minor modifications of existing systems has only increased confusion.

Briefly put, Dr. Dyson proposes a ciphering system so designed that it will provide for each organic compound a unique expression in the form of a linear arrangement of letters and Arabic numerals which will completely define its structure and be capable of translation at will into a structural formula. In the writer's opinion he achieves this end by a method which, although highly ingenious, is one of remarkable simplicity. Its success depends on the acceptance of certain predetermined rules for the enumeration of all the significant atoms in an organic structure. These rules are, however, simple and logical. For a description the reader is referred to the monograph itself, but some idea of them may be gathered from the statement that all fused ring systems (homocyclic and heterocyclic) are enumerated in terms of a few conventional ring systems, *e.g.* benzene, naphthalene, phenanthrene and anthracene, and all analogously constituted compounds are similarly enumerated; thus, for example, chrysene and *cyclo*pentenophenanthrene are both numbered similarly on the basis of their common phenanthrene nucleus, and not, as in current literature, on two entirely different and arbitrary systems. Apart from this acceptance of a definite enumeration system, the cipher does not in any way affect existing principles of nomenclature.

Dr. Dyson's monograph gives a concise account of his notation system, furnished with a wealth of examples of its application, so that it can be regarded as a complete guide to its use. It is true that the average chemist may be somewhat taken aback when, for example, he first sees phloroglucinol ciphered as B.1,3,5Q, but the advantages of this mode of expression rapidly become apparent. The main principles of the system are easily mastered and it can be readily used by any chemist after quite a short study.

Even on the grounds above indicated, the Dyson System would be of great importance and value, but it has other features which commend it further. The system of letters and numbers employed has been carefully chosen so that it is amenable to mechanical sorting and computation. Using the cipher, the structure of a compound, together with the key to its literature references, can be recorded on a punched card; automatic machines can manipulate such cards so as to sort them into indexing order, print the ciphers and references in list form, or compute and print molecular formulæ (each symbol in the cipher having a fixed numerical equivalent).

Automatic handling of this nature has many obvious advantages. It would enormously simplify literature searching if all compounds containing some particular structural feature could be sorted out rapidly from a huge stack of cards by an automatic device. Moreover, the use of such mechanical aids may make it possible to produce what must be the dream of all research chemists—a lexicon of the Beilstein type presenting the essential facts on all known compounds which will be up-to-date rather than, as at present, many years behind.

Here, then, is a book which should be read by all organic chemists, and one which may become a milestone in the history of the science. A unique yet relatively simple expression for each organic compound on the basis of a readily memorised system such as is offered by Dr. Dyson is something new and vitally important. In the reviewer's opinion this system should be studied closely, for if it can withstand the criticism of all chemists—and it has already been exhaustively tested by a number of eminent organic chemists—it ought to be at an early date adopted internationally and used not only for indexing purposes but for the compilation of an up-to-date reference work of the Beilstein type.

REVIEWS

MATHEMATICS

British Association for the Advancement of Science :

1. **Mathematical Tables, Part-Volume A. Legendre Polynomials.** [Pp. 42.] (8*s*. 6*d*.)
2. **Mathematical Tables, Part-Volume B. The Airy Integral.** Prepared by J. C. P. MILLER. [Pp. 56.] (10*s*., including Auxiliary Tables I and II.)
3. **Auxiliary Tables, Number I. Coefficients in the Modified Everett Interpolation Formula.** (6*d*. each or 5*s*. per dozen, postage extra.)
4. **Auxiliary Tables, Number II. Table for Interpolation with Reduced Derivatives.** (6*d*. each or 5*s*. per dozen, postage extra.)

(All tables published for the British Association at the University Press, Cambridge, 1946.)

THE high standard of the Mathematical Tables prepared by the British Association Committee is well-known and the principal task falling to the reviewer is to describe the contents of these new volumes. These do, however, depart from the usual form in that the present tables are issued as Part-Volumes, in paper covers, as they are not thought large enough to warrant publication as complete volumes. It is intended that such part-volumes shall eventually be combined into volumes, adding to the Association's main series of tables, to which they conform in respect of size of page and typography. Meanwhile inconvenience due to delay in making the tables available is avoided.

Part-Volume A contains tables of the Legendre Polynomials $P_n(x)$ for the following values of n and x:

$$n = 2(1)12, \quad x = 0(0{\cdot}01)6 \text{ and } n = 2(1)6, \quad x = 6(0{\cdot}1)11.$$

The design and compilation of the tables, begun in 1932, has been under the direction of Dr. L. J. Comrie. For $x < 1$, the values are given to seven decimals. Use has been made of existing tables by the British Association ($n = 5, 6, 7$), Tallqvist, and Hayashi ($n = 8$), though these have been carefully checked by differencing and comparison. Five errors were found in Hayashi's table. For $n = 10, 11, 12$, the polynomials have been computed from the definitions by Dr. A. J. Thompson. It may be noted here that the 6-figure tables of Associated Legendre Functions, recently issued by the New York Mathematical Tables Project, also give $P_n(\cos\theta)$ for $n = 1(1)10$, but with different arguments, as $\theta = 0°\ (1°)\ 90°$.

It is for $x > 1$ that the B.A. volume mainly breaks new ground, and the corresponding entries occupy 31 of the 37 pages of tables. The values are given to 7 (often 8) significant figures, with a few minor exceptions. Interpolation by Everett's formula is provided for throughout by the printing of

second differences, modified when necessary to allow for δ^4 and δ^6, although where δ^4 exceeds 1000 it is given also. Considering the authorship and care in preparation, these tables are certain to be most reliable.

Part-Volume B is concerned with solutions of the equation $y'' = xy$, important in applications of second-order equations $y'' = \rho(x)y$ in which $\rho(x)$ is approximately linear over a limited range. It first acquired interest when the regular solution, in integral form, was needed by Airy for some optical calculations in 1838. This work follows closely the development by Professor Harold Jeffreys, and uses the notation:

$$\mathrm{A}i(x) = \frac{1}{\pi}\int_0^\infty \cos\left(\tfrac{1}{3}t^3 + xt\right) dt$$

$$\mathrm{B}i(x) = \frac{1}{\pi}\int_0^\infty \left\{\exp.\left(-\tfrac{1}{3}t^3 + xt\right) + \sin\left(\tfrac{1}{3}t^3 + xt\right)\right\} dt$$

Following an historical introduction, there is a comprehensive description of the functions involved and of the preparation of the tables, by Dr. J. C. P. Miller. This repays careful reading. A graph and two pages of formulæ (including the relations between $\mathrm{A}i(x)$, $\mathrm{B}i(x)$ and the Bessel functions of order $\frac{1}{3}$) form a valuable summary.

The tables which follow contain

$\mathrm{A}i(x)$ and $\mathrm{A}i'(x)$	$x = -20(0{\cdot}01) + 2$
$\log_{10}\mathrm{A}i'(x)$ and $\mathrm{A}i'(x)/\mathrm{A}i(x)$	$x = 0(0{\cdot}1)25(1)\ 75$
$\mathrm{B}i(x)$ and reduced derivatives	$x = -10(0{\cdot}1) + 2{\cdot}5$
$\log_{10}\mathrm{B}i(x)$ and $\mathrm{B}i'(x)/\mathrm{B}i(x)$	$x = 0(0{\cdot}1)10$

The first 50 zeros and turning values of $\mathrm{A}i(x)$, and the first 20 of $\mathrm{B}i(x)$, are also given. Finally amplitude and phase functions $\mathrm{F}(x)$, $\chi(x)$, $\mathrm{G}(x)$, $\psi(x)$, defined by the relations

$$\mathrm{A}i(x) = \mathrm{F}(x)\sin\chi(x) \qquad \mathrm{B}i(x) = \mathrm{F}(x)\cos\chi(x)$$
$$\mathrm{A}i'(x) = \mathrm{G}(x)\sin\psi(x) \qquad \mathrm{B}i'(x) = \mathrm{G}(x)\cos\psi(x),$$

are tabulated for $x = -80(1) - 30(0{\cdot}1) + 2{\cdot}5$. The aim throughout has been to provide an 8-figure standard of accuracy for $\mathrm{A}i(x)$, $\mathrm{B}i(x)$ and their derivatives, this in turn requiring 6 decimals in the phases $\chi(x)$, $\psi(x)$.

Throughout most of the tables, interpolation is adequately catered for by the second differences provided. In certain parts, however, fourth and higher differences are so large that resort to an extended Everett formula is necessary; moreover, a special method of interpolation for $\mathrm{B}i(x)$ and $\mathrm{B}i'(x)$ is adopted. It is to facilitate these interpolations that the auxiliary tables described below have been provided with Part-Volume B.

The computations have proceeded under the direction of Dr. Miller, who must be congratulated on bringing this formidable task to completion.

The Auxiliary Tables are interpolation aids for use with any functions suitably tabulated, and are therefore printed separately on cards. Computers are sure to find them useful.

Number I contains coefficients for a modified Everett formula, in which both second and fourth differences have been simultaneously modified to take account of higher order differences. Thus, with co-operation from the table-maker, the user is assured of very accurate interpolation without more effort than the inclusion of fourth differences usually requires. The coefficients are given to 7 decimals at sub-intervals of 0·01.

Number II enables interpolation in a function $f(x)$ and its derivative to be made by the Taylor expansions

$$f(x + \theta h) = f(x) + \theta\tau + \theta^2\tau^2 + \ldots + \theta^n\tau^n + \ldots$$

and

$$hf'(x + \theta h) = \tau + 2\theta\tau^2 + 3\theta^2\tau^3 + \ldots + n\theta^{n-1}\tau^n + \ldots$$

when the reduced derivatives $\tau, \tau^2, \ldots$, defined by $\tau^n = \frac{h^n}{n!}\frac{d^n}{dx^n}f(x)$, are provided (*e.g.* Table IV, $Bi(x)$ in Part-Volume B).

The tables on the card provide coefficients at intervals of 0·01 in θ as follows:

$$\theta^n : n = 2, 3, 4 \text{ (exact)}; \quad n = 5, 6, 7 \text{ (curtailed)}$$
$$n\theta^{n-1} : n = 2, 3 \text{ (exact)}; \quad n = 4, 5, 6, 7, 8 \text{ (curtailed)}.$$

R. A. B.

The Advanced Theory of Statistics. Vol. II. By MAURICE G. KENDALL, M.A. [Pp. viii + 521, with 30 figures and 52 tables.] (London: Charles Griffin & Co., Ltd. 50*s*. net.)

THIS volume completes a work which will, perhaps, be in use as a standard text for many years to come. There is no doubt of the value of the two books as a consolidated statement of the concepts and techniques employed by statisticians in recent years. There is, indeed, at present no other work of so comprehensive a nature in existence.

The volume now published applies the fundamental results developed in the first volume to various fields of study. There are four chapters on theories of estimation; two each on analysis of variance, time-series, and the general theory of significance tests; and single chapters on common tests of significance, the design of statistical inquiries, regression, and multivariate analysis.

Estimation is treated with considerable thoroughness. The similarities and differences between rival theories are squarely and clearly stated. The author adopts a neutral attitude, and expresses the opinion that effective reconciliation of the different systems may be practicable.

The chapters on time-series provide a valuable summary of methods available in this difficult subject. Many recent developments in this field have been originated by Mr. Kendall. These now appear for the first time collected together, forming part of a useful outline of the present position of the subject.

The presentation of the procedures of the analysis of variance (and covariance) is carried out competently and with due regard for practical considerations. Even though a part of the chapter on the design of statistical inquiries is also concerned with the same subject, the impression remains that a fuller treatment might be desirable. This in no way detracts from the value of what has in fact been written; and considerations of space were probably of importance in limiting the scope of these chapters. A more thorough discussion of the construction of the fundamental "set-up," and of the position of analysis of variance tests in the general theory would, however, be of value. It may be remarked, also, that the allocation of Randomised Blocks to one of the chapters on analysis of variance, and Latin Squares to the chapter on design of statistical inquiries, seems somewhat arbitrary.

The chapters on general theory of significance tests comprise a systematic formal development of the Neyman-Pearson theory, together with a section

on the methods of E. G. Pitman. These chapters form a useful summary and explanation of the theories with which they are concerned.

The chapters on common tests of significance and on regression provide between them a nearly complete range of current statistical procedures, and should be particularly valuable for purposes of reference. Multivariate analysis is treated in a somewhat compressed manner, and the mathematical complexities tend to obscure the practical meaning of the results. The chapter on design of statistical inquiries has already been referred to. It provides a pleasing contrast to the highly mathematical atmosphere of the rest of the book. A longer chapter of this type, dealing in greater detail with methods of sampling in survey work, etc., would considerably increase the value of the book. It may be that the author considers that such details should be left to specialist reading. Mr. Kendall gives copious references for such reading at the end of each chapter of his book.

The fact that such further reading should be required indicates that a more accurate title for the book would be "An Introduction to Advanced Statistics." In fact, any one of the subjects dealt with in the present volume could well be the title of a full-sized book. The very comprehensiveness attempted by the author must therefore lead to an incomplete, though most able, account of each separate branch. This is, of course, no criticism of the author's work. It is merely a consequence of the fact that the entirety of the advanced theory of statistics is too wide-ranging to be within the scope of a two-volume treatise. Imagine attempting to write a book of the same size on "The Advanced Theory of Mathematics." If the reader is of the opinion that statistics is only a branch of mathematics the analogy may not be admitted, but here reader and reviewer would be in disagreement.

The present rapid growth of statistical theory is another reason for the necessary incompleteness of any book on advanced theory. Evidence of this is provided in the Addenda dealing with recent developments in the theory presented in Volume I. In view of this factor and the value of the present work it is to be hoped that new editions will be produced with reasonable frequency.

There are two small errors which the reviewer would like to see corrected in such further editions. Firstly the statement on page 6 that $[\Sigma(x - \bar{x})^2/(n - 1)]^{\frac{1}{2}}$ is an unbiased estimate of the standard deviation of a Normal population (it is its square, of course, which is an unbiased estimate of the population variance); secondly, the statement on page 308 that it is undesirable to have a greater chance of accepting the hypothesis when it is false than of rejecting it when it is true (the context shows that the word "rejecting" should be "accepting"). There are also a few printer's errors, but these are much scarcer than they were in Volume I.

One final grumble. There is an extremely useful Bibliography of 62 pages, but Gauss is not among the authors listed therein.

N. L. J.

A Manual of Operation for the Automatic Sequence Controlled Calculator. By the Staff of the Computation Laboratory. Annals of the Computation Laboratory of Harvard University, Vol. 1. [Pp. xiii + 561, with 17 plates and 44 figures.] (Cambridge, U.S.A.: Harvard University Press; London: Oxford University Press, 1946. 56s. net.)

THIS Manual constitutes a complete description and book of operating instructions for the above machine, which is one of the latest American

"calculating monsters." Its construction was inspired by Professor H. H. Aiken (Harvard) and executed by the foremost engineers of the International Business Machines Corporation. Thomas J. Watson, on behalf of the latter corporation, presented the machine to Harvard University, where, since May 1944, it has been in use on scientific work for the U.S. Navy under Professor Aiken (also Commander U.S.N.R.).

The essential component of the calculator is not the electronic valve (as with the "Eniac") but the relay circuit; in fact the machine is largely an assembly of standard Hollerith parts. The speeds with which the fundamental algebraic operations are performed are, therefore, of the order of seconds or tenths of seconds, *i.e.* about 100 to 1000 times slower than with the Eniac. On the other hand a (specially constructed) tape sequence control automatically sets the machine up, directs and controls the operation, with a considerable gain in convenience. Indeed, for the frequent mathematical operations, such as the solution of simultaneous equations, numerical quadrature, subtabulation, etc., a library of control tapes is being compiled; such calculations can, therefore, be repeated instantly with fresh data.

The units of the machine comprise: 72 storage counters (which can be split and linked) each capable of holding 23 digits, 60 switch-set registers for holding constants, 2 units performing up to 23-figure multiplication or division, and 3 special units forming log $(1 + x)$, 10^x (or e^x) and sines (or cosines) respectively. The method of calculating log $(1 + x)$ is to factorise $(1 + x)$ into 5 factors, 4 of which are selected automatically from a set of 35 standards whose logarithms are permanently stored in the machine, and a fifth for which x is smaller than 10^{-8} so that log $(1 + x)$ can be calculated from at most 6 terms of the log-series. Similar operations are performed by the "10^x"—and the "sine"—unit. Other series can be formed at will in units called interpolators, but these must receive their instructions (including the expansion coefficients) from prepunched operating tapes.

Answers calculated by the machine can be automatically tabulated by an electromatic typewriter in type amenable to photo-lithographic reproduction.

To the many interested in the art of computing who have not access to the machine the chief value of this manual lies in its detailed account of the possibilities of the relay circuit as a computing unit. A close study of the manual is highly recommended and will probably save a great deal of unnecessary thought, time and cost.

H. O. Hartley.

PHYSICS

Why Smash Atoms? By Arthur K. Solomon. Revised edition. [Pp. xii + 204, with 132 figures and plates.] (Cambridge, U.S.A.: Harvard University Press; London: Oxford University Press, 1946, 16*s*. net.)

Many will have read with pleasure and profit the first English edition of this book, published as a Pelican in 1945 and based on the 1940 American edition. The new edition contains the best features of the old, a very clear and readable account of the progress of atomic physics, with the addition of three chapters on atomic power and the atomic bomb. There are a number

of delightful new photographs. The last chapter of the Pelican edition (Physics—after the War) has been omitted in this.

Some of Dr. Solomon's enthusiasm for his subject and the thrill of carrying out research is reflected in the writing. The book can be recommended without reserve to all, from schoolboys to professors, including those who believe they have no interest in the subject. Atomic physics is expanding at a rate comparable with the energy available from nuclear fission, and we look forward to a long series of new editions of this book.

F. A. V.

An Introduction to Heat Engines. By E. A. ALLCUT. Second edition. [Pp. x + 288, with 170 figures.] (Toronto: The University of Toronto Press; London: Oxford University Press, 1946. 15s. net.)

AFTER many years of war-time economy standards in the production of British and American text-books, one may perhaps be forgiven for recording a feeling of æsthetic pleasure as one's first impression of Prof. Allcut's second edition of this book. This feeling is induced by the quality of paper, the many well-drawn diagrams, and the size of type which is readily legible.

The author sets out to survey the fundamental principles, both thermodynamical and mechanical, which underlie the design, performance and construction of Heat Engines of all sorts, but, in view of the prevalent trend in Canadian Industry, the emphasis is laid on Internal Combustion as opposed to Steam Plant, though the latter is by no means omitted. There can be little doubt that this overall object has been achieved, with the aid of a very large number of diagrams, photographs, and a lucid exposition of the text. An interesting chapter on the history of the Heat Engine helps to impress on the reader how small have been the changes in the underlying principles of our Prime Movers from the days of Heron's Aelopile, the first attempt at a reaction turbine, and yet how great have been the mechanical improvements of construction. Many of the problems of the designer of to-day can be traced back to the engines of Newcomen and Watt, and it may perhaps be regretted from a British point of view that more emphasis is not laid on the development of such current problems as condenser de-aeration and boiler circulation which have survived from those early days. On the other hand, the inclusion of economical data and graphs serves as a useful guide to the practical limits of theoretical design.

In any book of this nature the author is faced with the problem of how much mathematical theory to include, so as to enable a beginner to carry out a certain amount of numerical work. Prof. Allcut has decided, no doubt wisely, that any standard work on Engineering Thermodynamics will supplement his own brief references in this respect. But one might venture to suggest that it would be within the scope and object of such a book to include the conception of entropy as one of the basic ideas in Thermodynamics, especially as use is made of the terms adiabatic and polytropic. While this is, of course, included in standard works to which the author refers, it would have been useful to give the beginner an "Introduction" to this all-important function of the working fluid. The difficulties of a non-mathematical approach are not underrated, but such a presentation would surely contribute greatly to a general appreciation of modern developments.

Altogether, this is a pleasant book to read with a great deal of well-presented information. The many references in the text will be found of

value by the more ambitious reader, and many a student endeavouring to become acquainted with the Theory of Heat Engines would do well to devote some serious study to the development and practice of the subject as described by the author.

K. REICHMANN.

Electric Discharge Lamps. By H. COTTON, M.B.E., D.Sc., M.I.E.E. Vol. XII of a Series of Monographs on Electrical Engineering under the Editorship of H. P. Young. [Pp. xvi + 435, with 216 figures, including 12 plates.] (London: Chapman & Hall, Ltd., 1946. 36*s*. net.)

As far as the reviewer is aware, this is the first comprehensive book on the subject to be published in the English language. It is one of a series intended for electrical engineers, but the subject demands for real understanding a knowledge of various branches of physics not normally included (so far) in the courses for Higher National Certificate or degrees in Engineering. How, then, is the author to treat his subject? He could, perhaps, advise his reader to read first appropriate text-books and monographs on physics, and assume knowledge of fundamentals in discussing the behaviour and properties of electric discharge lamps. He might compromise by summarising the fundamental laws of physics later to be applied, giving references to proofs and background information. Professor Cotton, who is Head of the Department of Electrical Engineering at University College, Nottingham, has not used either of these methods, but has attempted, with great courage and energy, the difficult task of providing in one volume all the necessary fundamental physics to enable an electrical engineer trained in the traditional way to understand the chapters on the discharge lamp itself. The attempt is a valiant one, but, unfortunately, is not completely successful.

After a preface mainly on the history of lamp development, there are two chapters on the physics of radiation which could with advantage be condensed and re-written to eliminate some obscurities and a few errors. For example, emissive power is wrongly defined; Boltzmann's constant k is used for Stefan's constant and given two quite different values; the term "brightness" is not confined to visible radiation; and in some cases the text does not correspond with the diagrams. A short chapter on the structure of the atom and valency follows. Here the statement that atomic nuclei are made up of protons and electrons should be replaced by a note on the structure which has been accepted for a number of years.

Chapter IV is on thermionic emission, only four pages long but containing a number of mistakes. The data on work functions are in some cases fifteen years out of date, and do not correspond with the values given later in the book (p. 154). There is no mention of space charge. Chapter V is a straightforward one on motions of electrons and gas molecules, including the Maxwell-Boltzmann distributions.

Chapters VI and VIII give a detailed account of the origin and structure of spectra. These chapters would make difficult reading for those who have little or no previous knowledge of the subject, and a more concise treatment with greater emphasis on physical principles would probably lead to greater clarity and better understanding. There are some repetitions and obscurities and a few mistakes, notably Fig. 88. Chapter VII is on discharge phenomena (29 pages), and Chapter IX (28 pages) is called "Fluorescence," though a better title would be "Luminescence."

Chapters X and XI (165 pages) give an excellent account of practical discharge lamps and the control gear used with them. These chapters will be welcomed by all interested in the newer forms of lighting. The last chapter is effectively an appendix on colour, ending with a few wise remarks on the choice of lamps for various tasks.

The book is very well illustrated by diagrams and photographs, and useful references are given for further reading. The best features of the book are so good that we hope the author will be encouraged to recast some of the earlier chapters and also to remove a rather large number of slips and misprints for a second edition.

F. A. V.

CHEMISTRY

Le Problème de la Réactivité des Combustibles solides. By HENRI GUÉRIN. [Pp. viii + 222, with 85 figures.] (Paris: Dunod, 1945.)

FURTHER advances in the efficiency of the preparation and utilisation of solid fuels would be greatly assisted by a knowledge of the chemical kinetics of combustion reactions less obscure than that at present available. In spite of the millions of tons of cokes, charcoals and similar fuels consumed annually in a diversity of industries, agreement as to the best fuel to use for a particular process is seldom forthcoming, *e.g.* it is generally agreed that coke for blast furnaces must be of a minimum strength and of not too wide a size grading: there are, however, greatly different opinions as to whether or not the coke should react readily with oxygen. In view of the present stringency in the supplies of solid fuels and the consequent need for the highest efficiency in their utilisation, the publication of M. Guérin's book is opportune: he was commissioned to write it by a committee of the Centre d'Études Thermiques and has carried out the work in an eminently capable and scholarly manner. In the first three chapters the author differentiates and critically discusses in considerable detail the work already published on the reactivity of carbon with carbon dioxide (carboxy-reactivity), with oxygen (oxy-reactivity) and with water vapour (hydro-reactivity); Chapter 4 deals with attempts to assess the reactivity of coke indirectly. In Chapter 5 he endeavours to answer the question as to what extent variations in carboxy-, oxy-, and hydro-reactivity run parallel to each other; in spite of the extensive work in this field, there are not sufficient data to give an unqualified answer. The last chapters of the book are concerned with the various physical and chemical factors which determine the carboxy-reactivity of a coke. Altogether some 551 references are cited; the text is illustrated by numerous small but clearly drawn diagrams; the printing is good, but the paper is of poor quality. M. Guérin's book is unreservedly recommended to all concerned with the production and utilisation of solid fuel.

H. L. RILEY.

Oxidation. A General Discussion held by the Faraday Society, 1945. [Pp. 300.] (London and Edinburgh: Gurney & Jackson, 1946. 20*s.* net.)

THE crowded sessions of the Faraday Society Discussion on Oxidation held in September 1945 showed the high place this subject occupies in present-day chemistry and the reputation of the discussion meetings of the Society.

Research on oxidation has been greatly stimulated by new industrial processes, particularly the production of polymerised substances for plastics, by investigations on oxidation of rubber and unsaturated oils, and by work on the reactions in the internal combustion engine. The description of new experiments and theories and the cut-and-thrust of debate contained in this volume make it of value to the student who wishes to understand scientific method as well as to the specialist in the topic itself.

Most of the papers here published are devoted to the chase of the elusive "transient molecular species" which intervene between reactants and resultants in oxidations. Such intermediates may be monovalent radical ions, neutral radicals, or peroxides of various types. The simplest type of oxidation-reduction mechanism is the "electron-transfer" reaction as in the change : $Fe^{+++} + I^{-} \longrightarrow Fe^{++} + I$. Evidence that many organic oxidations are of this type is found in the transient deep colours sometimes observed (*e.g.* "benzidine blue"), and in relations between electrode potentials, activation energies and rates of reaction, and wave-mechanical "degrees of fixation of double bonds" of oxidations of hydroquinones, etc. In other oxidations the "dehydrogenation" theory may be preferred, *i.e.* that the first step is the removal of a neutral atom of hydrogen. How far such a mechanism may fruitfully be regarded as a combination of electron + proton transfer is still a matter for debate.

Many oxidation reactions have long chain processes initiated by free radicals. Over twenty years ago Backström pointed out that polymerisation by a radical mechanism was often coupled to oxidation processes. A new development, based on the simultaneous presence of oxidising and reducing agents added to the system, appears of great promise for initiating industrial polymerisation reactions.

Other topics discussed are the nature of the peroxides formed in olefine oxidation, recent work showing that the O_2 does not link across the double bond but adds to an adjacent CH group, and low and high temperature oxidations of hydrocarbons in general. It is now known that, in the direct attack of O_2 on saturated hydrocarbons, tertiary carbon atoms are the first point of attack. Many of the broad lines of the subject are now reasonably clear ; so much however remains to be done by future workers that we can expect an equally stimulating volume from the Faraday Society at some later date.

E. J. B.

Chemical Thermodynamics. By J. A. V. BUTLER, D.Sc. Fourth edition. [Pp. xvi + 569, with 109 figures.] (London : Macmillan & Co., Ltd., 1946. 12*s.* 6*d.*)

THE fourth edition of this work is bound in one volume instead of two and has been considerably revised and extended. An informative appendix on statistical mechanics (written by the late Dr. J. W. C. Orr) has been added and of other new matter one may mention particularly Chapter XVI on solubility and molecular interactions in solution. This contains, *inter alia*, a discussion of some of the properties of rubber solutions. The treatment is in general clear and easily understood and the development of each topic is illustrated by a large number of well-chosen experimental data. This is particularly noticeable in the sections on electrode processes and on surface films. A number of useful numerical examples is attached to each chapter.

The book, as a whole, demonstrates the range and variety of chemical topics in which thermodynamical methods have been applied with valuable results.

The treatment of temperature calls for some comment. It is stated on p. 246 that the thermodynamic scale of temperature agrees with the perfect gas scale. The latter is not defined and no further discussion is given of this fundamental conception. The discussion of partial quantities on pp. 300–14 is lucid and helpful but the term "chemical potential" is not used at all. In the reviewer's opinion it is also unfortunate that the symbol F has been chosen to represent Gibbs's Free Energy, as this is likely to lead to confusion and difficulty in the reading of many modern papers. The author is, of course, at liberty to use any symbolism and nomenclature that he wishes, but the value of his work to the reader is enhanced if he employs a nomenclature which is immediately understandable when it is encountered in the work of other writers.

Careful proof reading appears to have eliminated most misprints; one which appears to have escaped detection is the misspelling of "London" as "Loudon" on pp. 354 and 355.

S. SUGDEN.

The Chemistry of Heterocyclic Compounds. By AVERY A. MORTON. [Pp. viii + 549, with 73 figures.] (New York and London: McGraw-Hill Book Company, Inc., 1946. 30*s*. net.)

IN view of the great and rapidly increasing importance of heterocyclic compounds, the attention devoted to the study of the chemistry of these substances is frequently inadequate. There is a tendency to regard the heterocyclic branch of organic chemistry as very advanced and suitable only for study by a few specialists. Pyrrole, thiophen, furan, indole and quinoline compounds are probably included in the curriculum, but other heterocyclic compounds are usually encountered as individuals during special lectures on drugs, dyes, vitamins, alkaloids, etc., and the ring systems, as such, receive little, if any, adequate treatment. The vigorous growth occurring in heterocyclic chemistry renders such instruction out of date, and the properties of the various ring systems should now receive as much attention as the carbocyclic systems.

The appearance of Professor Avery A. Morton's text-book on *The Chemistry of Heterocyclic Compounds* is therefore most opportune in providing a modern and systematic account of the chemistry of these substances. The treatment is interesting and stimulating and a large amount of material has been skilfully condensed into the 550 pages. Numerous references to original work are provided and the problems included at the end of the chapters, whilst unusual in British works, encourage the reader to give further consideration to a number of instructive and related problems. On the whole the selection of material is excellent but Reddelien's explanation of Fischer's indole synthesis (p. 102) and the apomorphine synthesis (p. 317) are unworthy of inclusion in view of the severe criticisms to which they have been subjected.

The presentation of structural formulæ is, however, very disappointing. Penta- and trivalent carbon atoms are not infrequent in the work, important bonds are often omitted, the use of the symbol, R, for the benzene nucleus is of doubtful value, and many formulæ, *e.g.* atropine (p. 247), ecgonine and cocaine (p. 249), and hexamethylene tetramine (p. 516), are ambiguous,

unconventional and erroneous. Contrary to the statement on p. 343, the 3 : 4-benzphenanthridine synthesis outlined is quite unrelated to Pschorr's phenanthrene synthesis and the use of sodium pentoxide for $NaOC_5H_{11}$ (p. 109) is an unfortunate abbreviation.

The book can be recommended for undergraduates and research students, especially if it is realised at the outset that the work must be studied carefully, intelligently and critically. In spite of the defects, which it is hoped will be corrected in later editions, the book will fill a gap on the library shelves, where a volume on heterocyclic compounds has been urgently required.

R. D. H.

Vat Dyestuffs and Vat Dyeing. By M. R. Fox. [Pp. xii + 323, with 29 figures.] (London : Chapman & Hall, Ltd., 1946. 24*s*. net.)

New text-books on dyestuffs and the art of dyeing, particularly in English, have been conspicuously absent from publishers' lists for very many years in spite of the truly amazing technical advances which have been made in the last few decades. The appearance of this book, therefore, dealing with vat dyes, the aristocrats of the dyestuffs industry, is to be welcomed. One must also admire the courage of the author in attempting to deal adequately with both vat dyestuffs and vat dyeing in the limited space of 250 well-printed pages, but it must be admitted that in this he has attempted the impossible and the title is misleading. The book, which should have been entitled "The application of vat dyes," is written primarily for the practical dyer, on the assumption that the reader is devoid of any chemical knowledge even of the simple acids and bases, oxidising and reducing agents used in normal dyehouse practice, yet is perfectly familiar with the technical terms used in describing dyeing and finishing processes. By far the greater part of the book, approximately 170 pages, Chapters III–IX, describes the properties and the application of the various types of vat dyes, including the Indigosol or Soledon dyes and sulphurised dyestuffs of the Hydron Blue type, to animal, cellulosic and synthetic textile materials, by dyeing, padding and printing processes, and the various types of the numerous chemical assistants used in these processes are also described. Useful chapters on dyeing and printing machinery (adequately illustrated) and a short chapter on non-textile uses of vat dyes follow. The first two chapters dealing with vat dyes from an historical and chemical standpoint, however, are a great disappointment. They are completely inadequate and serve no useful purpose. They are, of course, meant to serve as an introduction to the subsequent chapters but they are scarcely referred to in the sequel; they would be definitely misleading to the student with the necessary chemical knowledge to appreciate them, and they will be practically meaningless to the person with no chemical knowledge. Special mention should be made of Chapters XII and XIII. The former, dealing with the identification of vat dyes, describes the author's own work and will be of interest to both chemists and colourists. It is an excellent summary of present knowledge and contains much that is new. The last chapter in the book is a very comprehensive list of commercial vat dyes, equivalents and dyes with similar properties being grouped together, and must certainly be of use to the practical dyer.

S. C.

Principles of Fruit Preservation. By T. N. Morris, M.A. Second edition. [Pp. xiii + 198, with 36 figures.] (London: Chapman & Hall, Ltd., 1946. 18s. net.)

The author of a treatise on scientific principles as related to industrial processes must necessarily experience difficulty in determining just how far it is possible to go with a description of the commercial processes themselves without diverging too widely from a strict adherence to his title. Dr. Morris in his book has kept a fair balance in most of his chapters, but one wishes that in dealing with certain aspects of fruit preservation he had gone into much fuller detail on the underlying principles and their scientific bases, even at the expense of the equivalent number of words given in the new edition to factory operations.

Although the author has brought the pectin story very much more up-to-date than was possible in his previous edition, there are numbers of points on which he is either too brief or completely silent. The calcium pectate method of analysis is described as being "used extensively in the past for accurate determinations of pectin" without drawing attention to the more recent work of Schneider & Bock, which presents this analysis in an entirely different light. The chapter on the composition of fruits is most disappointing. Fruits are extraordinarily variable in chemical composition, and the problems of processing are very closely bound up with the proportion of the various chemical compounds contained in the fruit, and yet one finds that the only table cited appeared in print in 1931, and merely gives highest and lowest figures without any reference to varieties or variations due to cultural or climatic conditions. The book does not pretend to refer entirely to English fruits, and in view of the enormous importance of citrus juices it would have been well if analyses of oranges and lemons, etc., had been included.

Dr. Morris has recognised the increasing importance of fruit juices as a new method of preserving fruit, but the chapter concerned deals almost entirely with practical methods, and one looks in vain for an examination of the principles which govern enzyme action, the suppression of yeast development, and other points which are fundamental to commercial production. The Boehi method of storage of juice is referred to, but the classical work of Jenny which provides the scientific basis for the process is not mentioned. The concentration of fruit juices is almost entirely given up to the freezing method which, whilst it undoubtedly provides the best product, is not in widespread use anywhere in the world, whereas the vacuum evaporator is treated with scant courtesy, although these plants exist throughout the world and have been responsible for the provision of practically the whole of the citrus juices sent to this country throughout the war, and also for enormous quantities of materials with high, natural vitamin-C contents which have protected children in the British Isles from deficiencies in their diet. The vitamin chapter is too slight to present the full story in detail. Fruits are recognised as most important sources of vitamin-C, and this chapter could with advantage have been much longer and given more references than is the case.

It is perhaps bad reviewing to pick out the points on which criticism is felt necessary and give them undue prominence at the commencement of the review. It has been done in this case only because the points mentioned are those which one would naturally expect to find in a book of this description.

The rest of the book is written in a clear and lucid style, and the scientific presentation of the various principles involved are clearly enunciated. No one wishing to undertake the processing of fruit could afford to be without this book, but its value would be greatly enhanced if it could be extended in certain directions to make it more comprehensive.

V. L. S. C.

Forensic Chemistry. By HENRY T. F. RHODES. Second edition. [Pp. viii + 164.] (London : Chapman & Hall, Ltd., 1946. 15*s*. net.)

THE second edition of the book adheres to the original division of the text which is divided into two principal parts, namely :—

(1) The Application of Chemical Methods to the Identification of the Person, and

(2) The Application of Chemical Methods to the Proof of Corpus Delicti.

The first part treats such subjects as the development of latent skin impressions, together with the classification, collection and chemical examination of occupational and other dusts.

Part 2 includes the examination of stains, firearms and explosives, questioned documents, counterfeit money, and toxic agents.

The subjects are dealt with in considerable detail, with some exceptions, notably the examination of toxic agents, to which subject only 22 pages have been allocated, with the result that the chapter in question is both fragmentary and unconvincing.

In the realm of Forensic Chemistry, the book covers a wide and ambitious field informatively. It also contains a broad review of relevant literature, largely French and German. The bibliographical references listed on pp. 157–160 number about 150.

Describing the examination of dust, the author devotes some two pages to the subject of chemical microscopy based on the principle of crystalline formation, but concludes with the statement that the method is not specific and has little more than a historical significance. He also describes Spot Reactions, but wisely considers that these are subject to many limitations. No allusion is made to spectrographic analysis, and in connection with dust collection there is no mention of Owen's Dust Counter.

The description of the examination of stains is open to criticism. On p. 51, the following statements are made in connection with the importance of confirmatory tests to establish the presence of blood : "In regard to confirmation, if the benzidene and leucomalachite reactions are positive, one of the micro-chemical tests, Strzyzowski's reaction as modified by Locard, should be applied. If this is also positive, it may be safely assumed that the stain is one of, or actually contains, blood." On p. 53, the author adds : "Iron and calcium salts interfere with Strzyzowski's reaction." Reference to spectroscopic examination is not made. It is highly doubtful if such findings would be viewed with acceptance in the British courts. On p. 53, touching upon the examination of seminal stains, it is stated that "a portion of the stain is soaked in 3% solution of silver nitrate for six hours. The stain is then washed thoroughly in one of the following solutions : . . . The stain is then again washed for half an hour in water. A portion of the stain is then carefully transferred to a microscope slide and mounted in the usual way. Spermatozoa are much more readily identified when stained in

this way than when they are unstained." What is meant by "a portion of the stain"? Does it mean a portion of the stained material, or an extract obtained from the stained material? If the former, how is microscopic examination to be made? If the latter, how is the extract to be dealt with during the process of staining? The description is anything but lucid in such respects.

The author has collected a considerable amount of information, much of which is not readily accessible, and this small volume should prove of use as a work of reference to research and other workers.

J. Glaister.

British Chemicals and their Manufacturers. [Pp. 121.] (London: Association of British Chemical Manufacturers, 1946. Gratis to purchasers of chemicals.)

This is a most useful book, incorporating the subject matter of the Association's two pre-war directories *British Chemicals and their Manufacturers* and *Directory of British Fine Chemicals*. It not only lists substances manufactured in this country, but also by means of a folder at the end of the book, and suitable reference numbers to each chemical, enables the reader to find at a glance the firm or firms from whom each substance can be obtained. It also includes a list of proprietary and trade names and of proprietary and trade marks. It is good to note that the next edition will be issued in 1948, and that the regular publication of this directory, suspended during the war years, is to be resumed. It will prove invaluable to all who use chemicals, either in industry or in academic circles.

F. P. D.

GEOLOGY AND GEOGRAPHY

La Paléogéographie : Essai sur l'Évolution des Continents et des Océans. By Raymond Furon. (Pp. 530, with 136 figures and 16 maps.] (Paris: Payot, 106 Boulevard Saint-Germain, 1941. Frs. 180.–.)

The book is divided into two parts, the first being introductory and general and the second palæogeographical. The first part is of particular interest to British readers; the striking examples chosen to illustrate methods and principles are drawn from the author's wide field of experience, and are therefore stimulating. Moreover, the stratigraphical table is essentially European, though partly American, and the British terms take their allotted place; terms less familiar to British students find a ready explanation. The account covers an enormous field, is lively and attractive; for example, the author illustrates problems of dispersal by referring, *inter alia*, to plants and animals carried by Man. Out-of-the-way subjects like the faunas of caves receive attention.

The second part deals with the continents and oceans in turn, from the Pre-Cambrian to the Quaternary. A sense of proportion is well maintained. Clearly the North Atlantic continent (Europe—North America) cannot be fully described in the 68 pages allotted to it; but the reader for whom the book is intended will gather all he wants in that amount of letter-press, and he will find it difficult indeed to get as much anywhere else with equal facility. The other continents are similarly dealt with; also the Atlantic, Pacific and

Mediterranean. Those who know the geology of their own continent well may regard its treatment as superficial, but will profit from accounts of the others. Selections of literature are added.

At the end of the book are systematic palæogeographical maps of the world, with the distribution of some faunas, facies, and other features. The author warns students in the text that these are in no sense precise—no such maps can be—but they give the average student exactly what he wants, namely, a well-informed general idea, and if he misuses them he must not blame the author.

The book is, on the whole, well illustrated. As the author has drawn on numerous sources, so his own sketch-maps and diagrams will no doubt find their way into other text-books.

The well-informed general reader, students of geology, and members of sciences other than geology will find this book both useful and interesting. Clearly it cannot be exhaustive in any part of the subject, and the author had no such intention.

K. S. S.

The Coastline of England and Wales. By J. A. Steers. [Pp. x + 644, with 114 text figures, 2 coloured plates and 115 half-tone illustrations.] (Cambridge: at the University Press, 1946. 42*s*. net.)

The coasts of Britain afford a remarkable diversity of origin and structure with rocks of most of the geological epochs reaching our shores, from the Pre-Cambrian of Anglesey to the recent deposits of East Anglia. They offer too clear evidence of the changes in relative level of sea and land in the raised beaches and submerged forests, whilst the evolution of divers types of recent coastal formation can be studied in the pebble beaches, dune systems and salt marshes. The Chesil Bank, where all sizes of material from the large stones near Portland to the finest sand near Burton Bradstock have been distributed by tidal action in perfect gradation, is as sublime a monument to the forces of nature as the combination of physical and biological activity that is displayed in a dune system such as that of Southport.

This work is essentially a physiographic description of our shores, conceived on a broad basis, which is valuable as an integration of the varied information acquired concerning the coasts of England and Wales from workers in many different fields. The author has himself visited a greater part of the coastline which he describes, and thus brings to his task a general knowledge of the whole, as well as his specialised familiarity with particular areas. The book opens with a brief general account of the geographical and geological features, whilst the greater part of the text is occupied with regional descriptions, though special chapters are devoted to sand dunes and salt marshes. The author would appear to be uncertain as to his precise audience, so that at times he is simple and clear, at pains to be non-technical, at others he uses terms that should for consistent treatment have been either avoided or defined. It is more a book of reference than a narrative and one which the visitor to the seaside as well as the serious student will find useful and informative. The numerous maps and photographic reproductions with which the text is embellished enable the reader to follow the descriptions of unfamiliar areas with ease.

Although reference is made to the vegetational features of the coasts, the author is obviously far less at home here than with the geological aspects

of his subject. The omission to treat of the many maritime species which are of peculiar geographical interest was perhaps in part desirable, on the grounds of safeguarding their preservation, but in the chapter on dunes it comes as a shock to find the long-lived *Lotus corniculatus* listed as an ephemeral and to find no mention of *Hippophæ rhamnoides* amongst the characteristic dune shrubs. But in so wide a topic as is compassed in these pages some slight blemishes are almost inevitable and the author has usefully filled a gap in physiographic literature.

E. J. S.

Géographie économique et sociale de la France. By PIERRE GEORGE. [Pp. 223, with 18 plates.] (Paris: Éditions Hier et Aujourd'hui, 1946. Frs. 135.–.)

SEVERAL works of outstanding merit have appeared in recent years on the political problem of contemporary France, but what is still seriously needed is a good, readable work in English on the economic and social structure of the country, since this is the basis of any real understanding of its life and problems. The work under review is intended to fill exactly this need for the French reader, and the author, a geographer, does it admirably. It opens with a brief survey of the physical build of the country (in which, perhaps, there are too many technical terms introduced in a few pages for the comfort of the general reader), but this is quickly followed by a cogent discussion of the demographic problem and of the need for making the best of the available man-power by the reduction of the incidence of tuberculosis and alcoholism, and by improving the standard of technical education. Here, too, arises the problem of absorbing the large non-French-speaking immigrant population, that made up 6 per cent. of the total population in 1936. The bulk of the book is devoted to three sections on agriculture, industry and commerce. After a survey of the general characteristics of agriculture and industry, there follows in each section a summary of the character of each of the main regions. The last section on commerce deals in turn with inland transport facilities, the tourist trade and foreign trade. It is a competent work and should be read by all those who are interested in the French problem.

R. E. D.

BOTANY

An Introduction to Botany. By A. W. HAUPT. Second edition. [Pp. xii + 424, with 289 figures.] (New York and London: McGraw-Hill Book Co., Inc., 1946. 17*s.* 6*d.* net.)

Botany. Principles and Problems. By EDMUND W. SINNOTT. Fourth edition. [Pp. xviii + 726, with 403 figures.] (New York and London: McGraw-Hill Book Co., Inc., 1946. 22*s.* 6*d.* net.)

THESE books are two well-known text-books of botany, both of which have recently been revised and republished, respectively as second and fourth editions. As text-books, each has deservedly achieved some reputation which is likely to be maintained by the present revised forms. It is, of course, true that most teachers of a subject have their own strong views as

to the most suitable form of text-book to employ and, while the reviewer would admit the virtues of each of these books, neither perhaps quite reaches the form which he would prefer.

The strong point of Dr. Haupt's book is the consistent treatment applied throughout to the morphological part of the subject. Although the functional aspects of morphology and anatomy are not neglected, the treatment of the physiological parts of the work is, on the whole, somewhat scanty and these subjects are treated incidentally and functionally rather than from the point of view of the processes involved. The illustrations throughout are extremely clear, comprising both line drawings and excellent photographs, and they include a good many unusual aspects of the subject. Their one weakness seems to be the fact that most of those dealing with anatomical subjects refer only to transverse sections and the conception of anatomical form as involving three dimensions is thereby lost. It may be urged in extenuation of these criticisms that a great deal is done well and that to add more would increase the size of the book out of all desirable limits.

The second of these books attacks the problem of botanical teaching from the somewhat broader point of view and, as is perhaps to be expected in view of its author's interest in genetics, it deals very much more fully with developmental and morpho-genetical aspects of the subject and it devotes a smaller proportion of available space to the morphological work. Here again, much of the physiological work, though given considerably wider treatment, is treated as part of the functions of the different organs, though a chapter is added dealing with metabolism, which precedes a later treatment of plant growth. The treatment of these subjects has been greatly extended in this edition to include references to such recent developments as the use of "tagged" atoms, genetics in *Neurospora*, viruses, vitamins and antibiotics as well as such aspects of growth as tissue cultures and allometric growth. This book is, therefore, on the whole, more suitable for the British degree student and perhaps its strongest point is the way in which the interrelationships of the different parts of the subject are developed.

W. H. P.

pH and Plants. An Introduction for Beginners. By JAMES SMALL, D.Sc., Ph.C., F.R.P.S., M.R.I.A., F.R.S.E. (Pp. viii + 216, with 16 figures.) (London: Baillière, Tindall & Cox, 1946. 12*s.* 6*d.* net.)

IT might be argued that the prominence which "*p*H" has been given in recent biological research and teaching is due more to the apparent ease with which it can be measured than to a real appreciation of the fundamental part which the hydrogen ion plays in physiological processes. Be this as it may, there is undoubtedly room for a book which will explain clearly to the botanist the basic physico-chemical concepts involved, and which will emphasise the complex way in which hydrogen ion concentration may interact with other factors of importance to plant life. Judging from its title, Professor Small has set out to supply this want in writing *p*H *and Plants. An Introduction for Beginners.* It cannot be said that he has succeeded. An account is given of the theoretical principles underlying the concept of *p*H, but too large a proportion of the book is taken up by detailed empirical information, often insufficiently evaluated and integrated. Thus the chapter

on pH and enzymes consists largely of a catalogue of the pH ranges within which various individual enzymes function and of an account of the part played by hydrogen ion concentration in the regulation of stomatal aperture in *Coffea arabica*. The effect of pH on enzyme action is not discussed in the light of modern knowledge of the nature of enzymes or even in relation to the effects on the properties of proteins mentioned in the preceding chapter. Similar criticism may be made of the other sections. The standard of draughtmanship shown in the diagrams and some of the tables is low and some of the figures are very obscure. The diagram representing the inter-relationships of the factors concerned in stomatal movement is an exception, presenting the essential facts in a neat and easily remembered way.

This book will be useful for reference, but it cannot be recommended for student use.

G. E. F.

La Culture des Tissus. By R.-J. GAUTHERET. Third edition. [Pp. 202, with 32 plates and 43 figures.] (Paris : Librairie Gallimard, 1945. Frs. 190.–.)

THIS book deals with plant tissue culture and, in a readable form, gives a good deal of information about the European results which have accrued from the application of this particular technique to plant growth. The manner in which the treatment is developed is interesting, because the author maintains throughout the point of view that he is dealing with a scientific problem, and he shows the way in which enquiry into this problem has developed. Taking it on the whole, his treatment deals first with the development of methods of growing plant tissues *in vitro* and then, secondly, with the nature of the morphological problems which arise in studying tissue cultures. He deals with the effect of growth-promoting substances and also with their physiological interpretation and, finally, considers the application of his findings to the problems of polarity in plant organs and the problems of plant pathology.

One of the difficulties of tissue culture work from a morphological point of view has been that while it is easy, with due precautions, to get tissues to grow in an unregulated fashion so that amorphous masses of more or less uniform cells are produced, little progress has been made with the problem of inducing such growth products to develop into organised tissues such as those found inside a typical plant. If an already organised plant growing-tissue is used as the inoculum, then it continues to develop in its existing form and, on the whole, its form is not greatly changed during growth in culture. In some tissues, as for example in cuttings from freely growing species like Horseradish, a completely undifferentiated callus may be formed which in due course develops, or may develop, roots or buds. This is, however, a well-known phenomena which depends on what we call the existing polarity of the tissue and it is evident that the polarity is carried over to the culture unchanged. The problem is, therefore, to find a technique by which organisation, in the sense in which it is applied to root and shoot growing points, can be imposed on freely dividing and undifferentiating tissues in culture. M. Gautheret clearly is approaching this problem and his mode of approach will be appreciated by those interested in these matters.

W. H. P.

Manuel d'Arboriculture fruitière. By E. Delplace. Third edition. [Pp. viii + 510, with 441 figures.] (Paris : Librairie Lamarre, 1945. Frs. 148.–. net.)

To produce such an encyclopædic work of pocket size on the practical aspects of fruit culture calls for a conciseness of expression which the practical man will appreciate ; nothing is lost by this mode of treatment, for the book is illustrated with numerous simple figures of almost diagrammatic clarity. The general treatment ranges from the raising of stocks, and grafting, to marketing, and insect and fungus pests. The second part of the book is concerned with the culture of individual fruits. Under the more genial climate of France, of course, peaches, apricots and grapes may be dealt with on the same terms as apples, pears and soft fruits, although wall culture is necessary in the north of the country and has claimed its share of attention.

An attempt has been made to describe the numerous varieties with which the text deals, but it may be doubted if the treatment is sufficiently full, even with the outline drawings, to make identification possible by any but the expert.

A third section of the book deals with the layout of gardens and orchards and also contains calendars for the harvesting and use of fruit.

To the beginner and amateur, at least, it would be difficult to suggest a more useful book of the same size, for he will encounter few problems which it will not help him to solve.

F. W. J.

ZOOLOGY.

Atlas des Parasites des Cultures. I. Généralités. Procédés de lutte anti-parasitaire. Étude des parasites : Orthoptères, Hémiptères, Névroptères, Lépidoptères. By Raymond Poutiers. [Pp. 127 with 12 coloured plates, and 51 figures.] (Paris : Editions N. Boubée & Cie., 1945. Frs. 200.–.)

Dr. Poutiers' *Atlas* is in three parts. Its aim is to enable growers and others interested to recognise the principal pests and diseases causing damage to cultivated plants of all kinds and to give the most appropriate control measures. Part I, the small volume under review, includes introductory sections and brief accounts of insects of economic importance in the orders Orthoptera, Hemiptera, Neuroptera and Lepidoptera. Thus a wide field is covered in a small compass and the treatment is necessarily very condensed. Remedial measures—biological, mechanical, cultural and chemical—are dealt with in 14 pages and an introduction to the morphology and biology of insects in 5 pages, the remainder of the text being devoted to short descriptive notes on a large number of species in the orders mentioned that feed on cultivated plants, and still briefer notes on means for their control. Many of the insects referred to do not occur in this country or are not sufficiently injurious here to be regarded as pests.

The book is packed with information in very concise form and will be useful for reference, but, for the practical grower, the lack of detail must inevitably be a serious drawback. The line drawings and the coloured plates, illustrating some of the pests and the damage they cause, may be helpful, though no indication is given as to the size of the insects depicted in the text figures ; for the readers for whom the book is intended, the space occupied by 10 figures of the pygidia of different species of Scale Insects could perhaps have been used to greater advantage.

C. T. G.

Biology of Tissue Cells. By ALBERT FISCHER. [Pp. viii + 348, with 55 figures.] (Copenhagen: Gyldendalske Boghandel; Cambridge: at the University Press; New York: G. E. Stechert & Co., 1946. 31*s*. 6*d*. net.)

THERE is a high probability of finding good reading in a book by Dr. Albert Fischer on tissue culture. In this instance one's anticipation of the fare is enhanced by its dedication—" to the memory of Jacques Loeb." Nor are these anticipations unfulfilled. The main theme is a discussion of the extent to which a tissue culture resembles an organism. Associated with this are somewhat detailed descriptions of the morphology of various cell types in tissue culture, and examinations of the exchanges between a cell and its environment, the nature of growth-promoting substances, the nitrogen metabolism of tissue culture cells, and of their energy exchanges. If there is a cause for complaint about this diet, it is not of lack of richness, but of lack of balance. As one reads, one is well aware of those courses which deeply interested Dr. Fischer: equally, one is aware of those which did not.

There are many grounds for scepticism of the theory that the cells of the metazoa are potentially quite independent units. The general nature of these grounds was summarised in J. Gray's book, *Experimental Cytology*. In this account of mammalian and avian cells Fischer moves almost to the opposite extreme, in this respect resembling Wigglesworth in his article on insect tissues in the Festschrift recently presented to Sir D'Arcy Thompson (*Growth and Form*). A tissue culture cannot be produced from one cell: the initial implant must consist of a number of cells. The cells have protoplasmic connections, which, though often constantly breaking and reforming, are essential for the well-being of the cells. If one cell dies, as by the action of a micro-dissection needle, neighbouring cells may die. Even the wandering cells make contact with one another far more frequently than is to be expected on a basis of random collisions. The ultimate size of a culture is often relatively independent of the size of the culture medium, and relatively dependent on the size of the initial implant. When part of a well-established culture is cut away, regeneration of the " wound " is rapid, and accompanied by relatively little growth of the uninjured part of the culture. Cell differentiation varies in a characteristic way in the different parts of a culture. It is on arguments such as these that Fischer bases his view, which is best summarised in his own words: " Tissue cultures must be regarded as regenerating tissue fragments, primitive cell states, or organism-like systems with strong correlations, and not as colonies of independent cell individuals."

J. F. DANIELLI.

L'Origine des Espèces. By ÉMILE GUYÉNOT. [Pp. 128, with 19 figures.] 1944. **Génétique et Hérédité.** By MAURICE CAULLERY. [Pp. 128, with 32 figures.] 1943. **La Genèse de l'Humanité.** By C. ARAMBOURG. [Pp. 136, with 36 figures.] 1943. **Comment se défend l'Organisme.** By LÉON BINET. [Pp. 120, with 12 figures.] Fourth edition, 1943. **Le Moteur vivant.** By PAUL CHAUCHARD. [Pp. 128, with 23 figures.] 1945. (Collection " Que sais-je ? " Presses Universitaires de France, Paris.)

THE extensive series of cultural handbooks, " Que sais-je ? ", published in France during the war, and covering a wide range of subjects, bears testimony to the keen interest in intellectual studies which was maintained

during the occupation. If we may judge by these five biological examples, the Collection reaches a very high level of competence and accuracy. Those under review are so good that they may be read with profit by the professional biologist as well as by the layman to whom they are primarily addressed.

Prof. Guyénot's account of the present state of evolution-theory is a little masterpiece of exposition; it is comprehensive, up-to-date and well balanced. The days are past of grandiose speculations and all-embracing theories of evolution; the modern attitude is more modest and more critical. Guyénot accepts the teachings of genetics, and considers that gene mutations may have played a considerable rôle in the formation of the smaller systematic groups. As to the origin of the groups larger than the species we know practically nothing, and "we must not forget that the world of life shows us without doubt something more than the result of unco-ordinated mutations arising by chance" (p. 112). We are still quite at a loss to understand the origin of a new organ or of a new structural type. Such is the conclusion of this admirable little book.

Prof. Caullery gives a full and detailed account of the modern science of genetics, stressing the capital importance of this for the practical study of heredity. His book forms a very useful introduction to the subject. He is a convinced adherent of the gene theory, and perhaps overstresses its significance, but, like Guyénot, he admits that mutations do not provide the key to evolution.

The much-vexed question of the descent of man is discussed by Prof. Arambourg in a very able way in the light of the most modern evidence from palæontology and prehistory. It is common ground that the line leading to man branched off early from the simian stock which gave rise to the gibbons and the anthropoid apes, but just how early is uncertain; Arambourg puts it about the base of the Miocene. In the genealogical tree sketched on p. 131 the descent of man is traced through *Limnopithecus* and forms resembling *Australopithecus* to pre-human types such as *Pithecanthropus* and *Sinanthropus*. The genus *Homo* first appears in the Quaternary in the form of Neanderthal man, who in turn gives place to the Cro-Magnon man of the Palæolithic, the immediate ancestor of modern man. Arambourg gives the whole evidence and discusses divergent views very fairly, and he has some wise remarks to make about the doubtful progress made by civilised man and the improbability of his developing into superman.

Prof. Binet discusses in a most interesting manner the subtle and delicate ways in which the organism, through physiological means, protects itself against adverse influences, such as cold, heat, pain, lack of oxygen, hunger and thirst, loss of blood. His very successful little book forms a useful supplement to the work of W. B. Cannon and his school described in that classic *The Wisdom of the Body*, especially as it gives an account of recent researches in France.

The mechanism of bodily movement, especially in man, and its control by the nervous system is the subject of Dr. Chauchard's little monograph. He describes the muscular architecture of the body in relation to the skeleton and the varied functions to be performed, and gives a full account of the contractile element of muscle and of the very complex physico-chemical processes underlying muscular contraction. A third section deals with the nervous impulse and the co-ordinating action of the central nervous system. Altogether a competent and up-to-date piece of work. It is interesting to

note that the author's point of view is non-materialistic; he refuses to believe that the marvellous and delicate adaptations of form and function which the body shows can be the fruit of chance.

E. S. RUSSELL.

MISCELLANEOUS

The Huxley Papers: A Descriptive Catalogue of the Correspondence, Manuscripts and Miscellaneous Papers of the Rt. Hon. Thomas Henry Huxley, P.C., D.C.L., F.R.S., preserved in the Imperial College of Science and Technology, London. By WARREN R. DAWSON, F.R.S.E., F.S.A. [Pp. xii + 201.] (London: Macmillan & Co., Ltd., 1946. 25*s.* net.)

THE examination and classification of these papers, which were acquired by the Imperial College in 1937, was by no means an easy task. They were in great disorder, owing, as the editor says, to the "utterly unsystematic, unbusinesslike and careless habits of Huxley in all that concerned his correspondence and papers." His handwriting was so "atrocious" that the papers demanded the most competent intuitive study before they could be deciphered. This deterioration from his earlier neat and legible script began in the later twenties of his life, and thenceforward became more and more pronounced as he advanced in years and commitments. The more important letters have now been bound in seven volumes, and the remaining correspondence and other papers have been sorted out and arranged by Mr. Dawson for binding in a further twenty-three volumes, when conditions permit. The letters include those written by Huxley himself, or sent to him. They are about 4500 in number, and comprise some 850 correspondents, which testifies to the wide range of the material, and to the catholicity of Huxley's interests and friendships. In addition to the letters there are other documents such as diplomas, diaries, caricatures, drawings and photographs, which, not being suitable for binding, are preserved in filing cases.

We must admire the skill and industry displayed by Mr. Dawson in identifying, classifying and epitomising all the items in this confused welter of manuscripts. The result of his labours is a printed catalogue which at first sight appears to be one of those works of reference of much value and even importance, but which is not intended to be read. This, however, would be a mistake, since a closer examination enables the reader to pick up some crumbs from Mr. Dawson's admirable miniature epitomes. A detailed index would have been a welcome addition, but its compilation might have broken the back of an already overwrought editor. It is obvious that we have in this volume a magnificent field awaiting exploration by some future Ph.D. candidate in the history of biological science during the Victorian era. New light would be thrown not only on Huxley's own activities and interests, but on the personalities of his contemporaries, and on the influence exercised by the Royal and other learned societies. There is thus much to be added even to the detailed biography of Huxley by his son Leonard.

The names of the correspondents are arranged alphabetically, and this to some extent takes the place of an index. The dates of birth and death of each writer are given and their letters are arranged in chronological order, the places of origin being also recorded. Press marks enable the student to

put his hand at once on any letters or documents wanted. The most voluminous of Huxley's correspondents were Hooker, Darwin, Michael Foster, Tyndall, Lyell, Dohrn, Haeckel, Herbert Spencer and Lankester. Wallace apparently was not addicted to letter writing, and it is surprising and disappointing that there are so few letters from W. K. Parker. Huxley constituted himself Parker's father confessor, and favoured him with admonitory advice of a most delightful character, but the incorrigible Parker, who had little gift of humour, could not be induced to mend his ways. It is pleasant to note that Huxley never despised or discouraged the amateur worker, as his letters to Albany Hancock and others abundantly illustrate. Several letters from and to that most lovable man George John Romanes relate to the Romanes lecture delivered by Huxley in the Sheldonian Theatre, Oxford, on May 18, 1893. The reviewer was present on that occasion, and was privileged to spend the morning with Mr. Romanes in Huxley's company. The great man talked incessantly, and with his customary vigour and charm. From time to time he pulled himself up, observing that he must nurse his voice for the lecture in the afternoon. These pauses, however, were of short duration, and the result was that the lecture was inaudible to many of the audience, and the undergraduates in the gallery, after urging him to "speak up," without obtaining the required response, clattered noisily down the stairs into the street. Huxley, unmoved, continued to the end, refusing to hand over to the Public Orator, who had previously conned over the lecture, and was prepared to read it if Huxley's voice should, as it did, fail.

The work is well printed on good paper, but the binding is suggestive of war-time craftsmanship.

F. J. Cole.

The Life of a Chemist : Memoirs of Vladimir N. Ipatieff. Edited by Xenia Joukoff Eudin, Helen Dwight Fisher and Harold H. Fisher. Translated by Vladimir Haensel and Mrs. Ralph H. Lusher. [Pp. xvi + 658, with 8 plates.] (Stanford University Press ; London : Oxford University Press, 1946. 33*s*. 6*d*. net.)

Among chemists, the reputation of Vladimir Nikolaevich Ipatieff rests securely upon a long and distinguished record of research work. His name is linked with the first synthesis of isoprene, which he accomplished in 1896 ; but he is more widely known as a pioneer in the investigation of catalytic reactions at high temperatures and pressures, upon which subject he published an authoritative book in 1936. As a chemist he takes rank with a select band of Russian masters, including Mendeleev and Lomonosov. The work under notice, which is issued as a publication in the Hoover Library on War, Revolution, and Peace, is concerned not so much with the details of Ipatieff's chemical researches as with the recollections of an eminent scientist who played a leading part in recent eventful years in Russian history.

Ipatieff, born in 1867, was intended for a military career. He reached the rank of major-general in 1910 ; but during his passage through the Mikhail Artillery Academy he was attracted intensely to chemistry, which thereafter became his chief interest. As he says of his half-brother, Chugaev, from that time he evidently "considered science his purpose in life." His chemical researches showed an originality so pronounced that in 1916 Ipatieff was made a member of the Russian Academy of Sciences. His work was not only of great theoretical interest, for high-pressure catalysis has done much

to revolutionise chemical industry in the twentieth century. As Ipatieff himself pointed out in 1927, apart from atomic structure, the leading chemical problems of this century have been catalysis, adsorption, and colloids, in three closely related fields.

Besides becoming a major-general and a professor at the Mikhail Artillery Academy, Ipatieff was a figure of the first magnitude in Russian science for some years before and after the Revolution. During the first World War he became the leading Russian authority on explosives and chemical warfare, and after the Revolution he threw himself into the gigantic task of directing the restoration and development of the disrupted chemical industries of Russia. During this intensive work over a long period he came into close contact with all sorts and conditions of men, ranging from the Tsar, Mendeleev, Lenin, and Trotsky to uneducated workmen whose remedy for recalcitrant blast-furnaces was to lower ikons into them!

This story of Ipatieff's life has no pretensions to literary merit. It is told in simple factual sentences which make it all the more convincing. Striving to keep clear of politics and to make his country's interests the first consideration, Ipatieff became in 1921 a non-Party member of the Soviet Government. By 1930, however, conditions affecting him had so deteriorated as to lead him to leave his country and continue his scientific work in the United States. As a consequence, he records that in 1937 his name was removed from the rolls of the Academy of the U.S.S.R., and the Soviet Government "forbade Russian chemists to mention my name in their scientific publications."

These memoirs remind one forcibly of Viscount Grey's reflection: "The history of the French Revolution, the experience in our own time of the Turkish and the Russian Revolutions, show that, bad as despotism is, doomed as it is to work its own ruin, the first-fruits of its overthrow are not love and liberty."

JOHN READ.

Middle East Science. A Survey of Subjects other than Agriculture. By E. B. WORTHINGTON. [Pp. xiv + 239, with 16 plates and 5 maps.] (London: H.M. Stationery Office, 1946. 7*s.* 6*d.* net.)

THIS is No. 2 in a series prepared for the Middle East Supply Centre, Cairo (M.E.S.C.), during 1943–45, of which the volume by Dr. B. A. Keen, F.R.S., *Agricultural Development of the Middle East*, is No. 1. Dr. E. B. Worthington, Director of the Freshwater Biological Association, was the member of the Scientific Advisory Mission to the Centre charged with study of biological problems related to non-agricultural resources.

Perhaps a better descriptive title of this important and very ably compiled report would be "A Survey of Scientific Problems in the Middle East," and Dr. Worthington describes his work as being concerned with problems related to the non-agricultural resources, including water resources, and problems with a biological basis affecting population. It is almost a model of what a report of this type should be. Dr. Worthington has done much more than compile a report. The present work not only surveys the present conditions affecting the lives of some sixty-nine millions of human beings, but also indicates the lines of investigations calculated to effect desirable changes in public services so as to improve the social and economic conditions in the

eighteen or more countries having unusually varied types of civilisations, political systems or backgrounds, religions, climates and resources.

The M.E.S.C. had to solve immediately urgent problems, of which not the least important was securing adequate means of livelihood during the war in the various countries, some of which had been under enemy control, and all were subject to difficulties arising from lack of transport preventing the importation of what had come to be considered as essential foodstuffs and manufactured goods. Had its work stopped there, the Supply Centre would have been amply justified by the success achieved; but the Scientific Advisory Mission of the Centre has done much more, and Dr. Worthington has shown the basis of the long-term policy for the successful development of these countries, which are destined to play an ever-increasingly important role in that politically rapidly changing part of the world.

Excluding agriculture, the bases of progressive improvement in the means of livelihood and healthy living conditions in the various countries are all considered in their turn. There is obviously urgent necessity for the introduction in many parts of more scientific methods for completing surveys, for more detailed study of the geology, meteorology and all types of water supply, which are complementary to each other, if the problems relating to plants, animals, forestry and fisheries are to be studied and successfully solved.

In addition, there is the enormous field of the study of human diseases, both endemic and epidemic, and of public health and medical services, which looms so largely in any survey of tropical and sub-tropical countries; and closely related are the problems of nutrition, unusually difficult amongst such widely diverse types of peoples, amongst whom deficiency diseases are frequent with their inherent effects on human development and progress.

Dr. Worthington's well-documented addition to the series of publications from the M.E.S.C. is comprehensive and will be found unusually valuable to all whose public work lies or will lie in any of the countries with which the survey deals.

C. S. Gibson.

BOOKS RECEIVED

(*Publishers are requested to notify prices.*)

An Index of Mathematical Tables. By A. Fletcher, M.A., Ph.D., J. C. P. Miller, M.A., Ph.D., Lecturers in Applied Mathematics, and L. Rosenhead, Ph.D., D.Sc., Professor of Applied Mathematics, University of Liverpool. London: Scientific Computing Service, Ltd., 1946. (Pp. viii + 451.) 75*s*. net.

Fundamental Theory. By Sir A. S. Eddington, O.M., F.R.S. Cambridge: at the University Press, 1946. (Pp. viii + 292.) 25*s*. net.

Time and Thermodynamics. By A. R. Ubbelohde. London: Oxford University Press, 1947. (Pp. viii + 110.) 6*s*. net.

Methods of Mathematical Physics. By Harold Jeffreys, M.A., D.Sc., F.R.S., Reader in Geophysics, University of Cambridge, and Fellow of St. John's College, and Bertha Swirles Jeffreys, M.A., Ph.D., Fellow and Lecturer of Girton College. Cambridge: at the University Press, 1946. (Pp. x + 679.) 63*s*. net.

Analytical Experimental Physics. By Harvey Brace Lemon, Professor of Physics, and Michael Ference, Jr., Associate Professor of Meteorology and Physics, the University of Chicago. Second edition. U.S.A.: University of Chicago Press; Great Britain and Ireland: Cambridge University Press, 1946. (Pp. xvi + 588, with 66 plates and 584 figures.) De Luxe edition, 44*s*. Trade edition, 33*s*. net.

Antennæ. An Introduction to Their Theory. By J. Aharoni. Oxford: at the Clarendon Press, 1946. (Pp. viii + 265, with 149 figures.) 25*s*. net.

The Physical Principles of Wave Guide Transmission and Antenna Systems. By W. H. Watson, Professor of Mathematics in the University of Saskatchewan. Oxford: at the Clarendon Press, 1947. International Monographs on Radio. (Pp. xiv + 208, with frontispiece and 95 figures, including 2 plates.) 20*s*. net.

Principles of Radar. By Members of the Staff of the Radar School, Massachusetts Institute of Technology. Second edition. New York and London: McGraw-Hill Book Company, Inc., 1946. (Pp. 887, with 565 figures.) 25*s*. net.

Principles of Technical Electricity. By M. Nelkon, B.Sc., A.K.C., William Ellis School, London. London and Glasgow: Blackie & Son, Ltd., 1946. (Pp. viii + 240, with 190 figures.) 17*s*. 6*d*. net.

A Course of Reinforced Concrete Design. By Thomas J. Bray, M.I.Struct.E., M.Inst.B.E., past Lecturer on Reinforced Concrete to Derby Technical College, Derby. London: Chapman & Hall, Ltd., 1946. (Pp. viii + 216, with 76 figures, including 1 plate, and 25 charts and graphs.) 25*s*. net.

General Chemistry. By Eugene P. Schoch, Professor of Chemical Engineering, William A. Felsing, Professor of Chemistry, and George W. Watt, Professor of Chemistry, the University of Texas. Second edition. New York and London: McGraw-Hill Book Company, Inc., 1946. (Pp. xiv + 540, with 150 figures and 50 tables.) 20*s*. net.

Laboratory Experiments in General Chemistry and Qualitative Analysis. By George W. Watt, Professor of Chemistry, the University of Texas. International Chemistry Series. New York and London: McGraw-Hill Book Company, Inc., 1946. (Pp. 223, with 47 figures.) 10*s*. net.

Inorganic Syntheses. Vol. II. Editor-in-Chief, W. Conard Fernelius, Purdue University. New York and London: McGraw-Hill Book Company, Inc., 1946. (Pp. xii + 293, with 25 figures.) 20*s*. net.

An Introduction to Quantitative Inorganic Analysis. By Ronald Belcher, F.R.I.C., M.Inst.F., Scientific Officer, British Coke Research Association, and M. B. Thompson, B.Sc., Ph.D., A.R.S.M., Head of the Department of Metallurgy and Chemistry, Rotherham Technical College. London and Glasgow: Blackie & Son, Ltd., 1946. (Pp. xii + 160, with 15 figures.) 5*s*. 6*d*. net.

The Elements of Physical Chemistry. By F. W. Goddard, M.A., F.C.S., Senior Science Master, Winchester College, and E. J. F. James, M.A., D.Phil., High Master, Manchester Grammar School. Second edition. London, New York, Toronto: Longmans, Green & Co., 1946. (Pp. viii + 251, with 67 figures.) 6*s*.

Oxidation. A General Discussion. Reprinted from the *Transactions of the Faraday Society*, Vol. XLII, Parts 3 and 4, 1946. London and Edinburgh: Gurney & Jackson, for the Society, 1946. (Pp. 99–395, with numerous figures.) 20*s*. net.

The Mechanism of Contact Catalysis. By R. H. Griffith, D.Phil., Senior Research Chemist, the Gas Light & Coke Co. Second edition. London: Oxford University Press, 1946. (Pp. xii + 273, with 97 figures and 42 tables.) 21*s*. net.

The Chemical Kinetics of the Bacterial Cell. By C. N. Hinshelwood, F.R.S., Dr. Lee's Professor of Chemistry in the University of Oxford. Oxford: at the Clarendon Press, 1946. (Pp. x + 284, with 1 plate and 79 figures.) 20*s*. net.

Characterisation of Organic Compounds. By F. Wild, M.A., Ph.D., F.R.I.C., Fellow and Tutor of Downing College, Cambridge. Cambridge: at the University Press, 1947. (Pp. viii + 306, with 11 figures.) 18*s*. net.

A New Notation and Enumeration System for Organic Compounds. By G. Malcolm Dyson, M.A., Ph.D., F.R.I.C., Technical Director, Genatosan Ltd., Loughborough. London, New York, Toronto: Longmans, Green & Co., 1947. (Pp. iv + 63.) 7*s*. 6*d*. net.

British Chemicals and their Manufacturers. The Official Directory of the Association of British Chemical Manufacturers. Published by the Association, 1946. (Pp. 121.) Gratis to purchasers of chemicals.

Chemicals from Methane. By J. P. Lawrie, Ph.D. London: Science Services, Ltd., 1947. (Pp. 23, with 7 figures.) 3*s*. net.

X-Rays in Research and Industry. By H. Hirst, Nat.Phil.D., B.Sc.(Eng.), A.M.I.E.E., F.Inst.P., Assistant Director of Metallurgical Research, University of Melbourne. Second edition. London: Chapman & Hall, Ltd., 1946. (Pp. viii + 124, with 82 figures and 13 tables.) 13*s*. 6*d*. net.

Controlled Atmospheres for the Heat Treatment of Metals. By Ivor Jenkins, M.Sc., Member of the Research Staff of the General Electric Co., Ltd., Wembley, England. London: Chapman & Hall, Ltd., 1946. (Pp. x + 532, with 268 figures, including 54 plates, and 69 tables.) 50*s*. net.

Metallurgical Materials, Alloys and Manufacturing Processes. By V. N. Wood, A.M.I.B.F., Chief Metallurgist, Messrs. Hale & Hale (Tipton), Ltd., Dudley Port, Staffs. London: Chapman & Hall, Ltd., 1946. (Pp. xii + 340, with 287 figures, including 33 plates.) 25*s*. net.

Plastics for Production. By Paul I. Smith. Second edition. London: Chapman & Hall, Ltd., 1946. (Pp. xvi + 216, with 13 plates.) 15*s.* net.

The Dyeing of Textile Fibres. By R. S. Horsfall, M.Sc., and L. G. Lawrie, A.R.I.C. Second edition. London: Chapman & Hall, Ltd., 1946. (Pp. x + 438.) 25*s.* net.

The Nation's Food. A Survey of Scientific Data. Edited for the Society of Chemical Industry (Food Group) by A. L. Bacharach, M.A. (Cantab.), F.R.I.C., and Theodore Rendle, F.R.I.C. London: Society of Chemical Industry, 1946. (Pp. xviii + 349, with 4 plates, 12 figures and 133 tables.) 18*s.* net.

Mother Earth. Being Letters on Soil addressed to Sir R. George Stapledon, C.B.E., M.A., F.R.S. By Gilbert Wooding Robinson, M.A., Sc.D., Professor of Agricultural Chemistry, University College of N. Wales, Bangor. Reprint. London: Thomas Murby & Co., 1947. (Pp. viii + 201, with 8 figures, including 2 folding plates.) 9*s.* 6*d.* net.

Limestones of Canada. Their Occurrence and Characteristics. Part V. Western Canada. By M. F. Goudge. Canada: Department of Mines and Resources, Mines and Geology Branch, Bureau of Mines, No. 811. (Pp. x + 233, with 40 plates and 2 maps in pocket.) 50 cents.

The Coastline of England and Wales. By J. A. Steers, President of St. Catharine's College, Cambridge, University Lecturer in Geography. Cambridge: at the University Press, 1946. (Pp. x + 644, with 64 plates, including 2 coloured, and 114 figures.) 42*s.* net.

Introduction to Plant Ecology. By A. G. Tansley, M.A., F.R.S., Honorary Fellow of Trinity College, Cambridge, Sherardian Professor Emeritus of Botany, Oxford. London: George Allen & Unwin, Ltd., 1946. (Pp. 260 with 15 figures.) 8*s.* 6*d.* net.

Plant Ecology and the School. By A. G. Tansley, M.A., F.R.S., and E. Price Evans, M.Sc., L.C.P. London: George Allen & Unwin, Ltd., 1946. (Pp. 97, with 10 figures.) 6*s.* net.

Principles of Animal Biology. By A. Franklin Shull, Professor of Zoology in the University of Michigan, with the collaboration of George R. Larue, Professor of Zoology, and Alexander G. Ruthven, President, University of Michigan. Sixth edition. New York and London: McGraw-Hill Book Company, Inc., 1946. (Pp. xii + 425, with frontispiece and 305 figures.) 20*s.* net.

Dynamische Reaktionspathologie. Von K. v. Neergaard, Professor an der Universität Zürich, Direktor der Klinik und Poliklinik für physikalische Therapie. Basel: Benno Schwabe & Co., 1946. (Pp. 317, with 25 figures.) Swiss Frs. 24.–.

The Life of a Chemist. Memoirs of Vladimir N. Ipatieff. Edited by X. J. Eudin, H. D. Fisher and H. H. Fisher. Translated by V. Haensel and Mrs. R. H. Lusher. Stanford University, California: Stanford University Press; London: Oxford University Press, 1946. (Pp. xvi + 658, with 8 plates.) 33*s.* 6*d.* net.

Im Kampf um Wissen und Wahrheit. Sammlung "Wissen und Wahrheit", herausgegeben von der Gesellschaft für Wissen und Wahrheit, Nr.2. Bern: Verlag Hans Huber, 1946. (Pp. 133.) Swiss Frs. 6.20.

Anthology of Errors, with Comments. By Adam Gowans Whyte, B.Sc. London: Chaterson, Ltd., 1947. (Pp. x + 70.) 5*s.* net.

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SCIENCE PROGRESS

THE IMPORTANCE OF THE FOSSIL AUSTRALOPITHECINÆ IN THE STUDY OF HUMAN EVOLUTION

By W. E. Le Gros Clark, M.A., D.Sc., F.R.S.

Dr. Lee's Professor of Anatomy in the University of Oxford

In 1924 a most remarkable palæontological discovery was made by Professor Raymond Dart of the Witwatersrand University, Johannesburg. It consisted of an excellently preserved portion of the skull of an immature creature of ape-like appearance, together with an almost complete natural endocranial cast. The whole of the milk dentition and also the first permanent molar teeth were in position. The specimen was embedded in a limestone matrix, derived from a cave deposit at Taungs in Bechuanaland. Dart recognised in this fossil an astonishing combination of superficial simian features with morphological details of a hominid character. He proposed to allocate it to a new genus of the Hominoidea, *Australopithecus*, and regarded it as evidence of a very early phase in the evolutionary origin of Man. However, his views did not gain general acceptance; indeed, some authorities expressed the opinion that *Australopithecus* was nothing more than a variety of anthropoid ape closely akin to the gorilla and chimpanzee, and, while they admitted certain curiously human features in the skull and dentition, they suggested that these were probably an expression of parallel or convergent evolution and thus only of secondary importance. But in 1936, and during subsequent years, the remains of adult representatives of the same type of creature were discovered by Dr. Robert Broom of the Transvaal Museum, Pretoria. Some of these remains, which consisted of fossil skulls and limb bones, were found in limestone deposits at Sterkfontein (about 40 miles from Johannesburg) and allocated by Broom to a new genus, *Plesianthropus*; others were found at Kromdraai (about 2 miles from Sterkfontein) and allocated to another genus *Paranthropus*. Together with *Australopithecus*, these genera have now been included by Gregory and Hellman (1939) in a common sub-family, the Australopithecinæ. At the end of 1946,

a comprehensive monograph on the Australopithecinæ was published by Broom and Schepers. The data recorded in this monograph immediately made it clear that Dart's original interpretation of the significance of *Australopithecus* had been correct in all essential points and that the importance of the Australopithecinæ was far greater than many anatomists had believed it to be. Indeed, it is now clear that they have a profound significance for the study of the evolutionary origin of Man, and it is not too much to say that, in this respect, they represent by far the most important discovery ever made in the field of human palæontology. Recently, the present writer (in connection with a visit to Africa as a delegate to the Pan-African Congress on Prehistory) had the privilege of making a personal study of all this fossil material, and the present communication is based on his own observations as well as on the detailed information already published by Dart, Broom and Schepers.

Before entering on a discussion of the significant morphological features of the Australopithecine fossils, it is necessary to review briefly the general conceptions of human phylogenesis which have been current for many years now. It has been well recognised, of course, that on purely morphological grounds the modern anthropoid apes (constituting the family Pongidæ) are more closely akin to man than any other group of existing primates. Not only are the structural resemblances between the Pongidæ and Hominidæ remarkably precise and detailed in many anatomical features, such as those of the brain, skull, dentition, post-cranial skeleton, visceral organs, placentation, etc., but some of the physiological resemblances are almost equally striking (see Zuckerman, 1933). Thus it is clear that, in contradistinction to the other primates, the Pongidæ and Hominidæ form a natural zoological group, and this has now received final recognition (in the most recent classification of the Mammalia—Simpson, 1945) by the inclusion of the two families in one super-family, the Hominoidea.* But this conception of zoological relationship has also tended to carry with it the assumption that, since the anthropoid apes evidently represent a lower level of evolution so far as certain features are concerned (especially the relative degree of cerebral development), Man himself was originally derived in the course of evolution from an ancestral stock bearing many of the characteristic morphological traits found in the large anthropoid apes of to-day.

* In this essay, the term *hominoid* is used in adjectival form referring to the super-family Hominoidea. The term *hominid* is used in reference to the family Hominidæ (which includes all the living and extinct types of Man).

The main anatomical features which distinguish the Pongidæ as a natural group can be quite briefly summarised. In the larger representatives of this family, the brain is very similar in its convolutional pattern to that of Man, but it is only about a third of the volume. The jaws are massive. The dentition is characterised by a considerable enlargement of the incisors and canine teeth, the latter (particularly in males) forming sharp, projecting tusks. Associated with this is a powerful development of the temporal musculature, usually marked by strong bony ridges or crests on the skull. The foramen magnum and occipital condyles occupy a relatively posterior position on the base of the skull, and the nuchal musculature is strong and has an extensive attachment to the occipital region in order to counterbalance the weight of the front part of the head with its massive jaws. The arms are long and powerfully developed in adaptation to arboreal habits, which include the method of progression by swinging from bough to bough (brachiation). The legs are relatively short and the foot is provided with a mobile and opposable hallux. The question now arises—how far are these anthropoid ape characters *primitive* in respect of the Hominidæ? Certainly the small brain is to be regarded as a primitive feature, and there can be no reasonable doubt that the brain of a gorilla or chimpanzee represents a very close approximation to that of the ancestral stock which gave rise to the human family. But are the other features mentioned above necessary concomitants of this phase of evolution? It is probably fair to say that such a conception has been quite widely accepted for many years. It has been generally assumed, for example, that the immediate ancestors of the Hominidæ were almost entirely arboreal in habitat, showing much the same arboreal adaptations as the modern chimpanzee, and that one of the first stages in human evolution was marked by a "descent from the trees" and a gradual modification of a limb structure previously adapted for brachiation to a limb structure adapted for terrestrial progression in an erect posture.

Objections to this provisional picture of the evolutionary origin of Man have from time to time been raised by comparative anatomists, who have pointed out that in respect of some of their main anatomical characters the large Pongidæ are in fact more highly specialised than the Hominidæ. For example, the primitive form of the canine in the primates is believed to have been a "brachydont" tooth of moderate dimensions, more like that of certain primitive representatives of the Hominidæ, while in the limb proportions Man is certainly more primitive than the large anthropoid apes. Those who argue along these lines have based their reasoning partly on the

conception that the process of evolution has on the whole been marked by an orderly, regular and progressive sequence of changes dependent upon definite laws, and is by no means a haphazard or erratic phenomenon involving abrupt deviations and oscillations in the main direction of morphological development. But they have also been influenced by the so-called "Law of Irreversibility of Evolution" or "Dollo's Law." Now, it is important to emphasise that this "law" cannot be taken to imply a rigid uniformity in evolutionary procedure (which, of course, could only be proved by the most exhaustive analysis of large numbers of complete records of phylogenetic sequences); it was intended merely as the formulation of what appears to be a general tendency, so far as this is indicated by the relatively incomplete records which are so far available. These records, indeed, do suggest that, on the whole, evolution is irreversible in the sense that, once a certain stage of development is reached, a previous stage is very unlikely ever to be *exactly* reproduced again. But it is necessary to make a clear distinction between what may be called a "negative reversal" or the loss of a character which has previously been developed, and a "positive reversal" or the development anew of a character which has previously been lost. Negative reversals have, of course, been quite frequent occurrences in evolution, but it is probably true to say that they not uncommonly leave behind indications which are to be detected by detailed anatomical or embryological studies. For example, a number of muscles which were presumably present in a primitive phase of primate evolution have disappeared in Man, but their history is betrayed by fibrous vestiges, or by their occasional appearance as "atavisms" in individuals. Again, in many mammalian groups, one or more toes have been lost in the course of evolution, but their traces remain as vestiges in the adult or in the embryo. On the other hand, a positive reversal, in the sense that a lost character is again reproduced *in precisely its original form* is probably a very rare phenomenon, though even this is by no means theoretically impossible. The "law of irreversibility," therefore, can only be taken as a general guide in attempting to visualise evolutionary lines of development, and for this purpose it is extremely useful as an indicator of probabilities.

Let us now consider some of the distinctive characters of the large anthropoid apes in a little more detail. It has been argued that the brachiating method of locomotion has been an important factor in orientating the body to an orthograde rather than a pronograde posture, leading to various changes (in which the Pongidæ resemble the Hominidæ and differ from the lower primates), such

as in the arrangement and suspension of the viscera and the modification of the pelvic skeleton, and that this change of body orientation was in fact an essential prerequisite to the ultimate development of the erect posture in Man. Unfortunately for this theory, however, the habit of brachiation also leads to profound changes which are definitely opposed to those which have found expression in human phylogenesis. Not only does it lead to a great lengthening of the arms and a relative dwindling of the hind limbs, it also leads to certain quite well-marked degenerative changes. For example, the thumb undergoes a relative atrophy, accompanied by retrogressive changes affecting some of the muscles which control its finer movements. This specialisation is directly related to the adaptation of the hand and fingers as a kind of hook which permits the animal to swing very rapidly from branch to branch. It is this sort of comparative anatomical evidence which makes it improbable that Man (who shows no signs of such aberrant specializations) could have been derived from an ancestral stock already showing these extreme adaptations to brachiating habits. Characteristic changes also occur in the hind limbs of brachiators, for they become more specialised for grasping purposes than in the lower primates and thus relatively less capable for use in terrestrial progression. It is true that the gorilla and chimpanzee can "stand up" in the sense that they can temporarily balance themselves on their hind limbs, but this is by no means an habitual posture and is only resorted to occasionally and momentarily as, for instance, when the animal is on the ground and needs to free the arms for attack or defence. There is good evidence that the human foot was originally derived from a prehensile foot with a mobile hallux, such as is characteristic of lower primates; this is evidenced by the disposition of the musculature of the big toe in Man and also by the line of the functional axis of the foot (Morton, 1924). But the evolutionary conversion of an arboreally adapted foot, similar to that of the modern large anthropoid apes, into a human type of foot would offer such serious mechanical difficulties that it can hardly be considered feasible. This matter has been discussed in great detail by Morton, who has shown that, in a large and heavy animal such as the gorilla, the change from an arboreal to a terrestrial mode of progression tends to lead to a characteristic distortion of the tarsal elements of the foot, owing to the fact that, as the result of the powerfully developed arms and shoulders, the centre of gravity of the body is so placed that the body weight is bound to be directed mainly forward to the front part of the foot rather than back towards the heel. This distortion has been avoided in the human foot, and from such

considerations Morton argues that the human line of evolution must have diverged from the line of the modern anthropoid apes at a time when the common ancestor was a relatively small and agile type of animal, perhaps not much larger than the modern gibbon. If these arguments are valid, it follows that a terrestrial habitat must have been assumed by the ancestors of modern Man much earlier than has often been supposed. This conception receives some support of an indirect nature from a consideration of the remains of early Man in China—*Pithecanthropus* (*Sinanthropus*) *pekinensis*. Some fragments of limb bones of this primitive hominid have been discovered and, so far as they go, they indicate that *Pithecanthropus* was equipped with a limb skeleton identical with that of *Homo sapiens*, even in the refinements of its structure. Since it seems certain that this extinct genus of the Hominidæ lived in the Early Pleistocene, probably more than half a million years ago, it is clear that even at that remote time limbs of modern human type had already been acquired, though the brain, skull, and dentition still retained many remarkable simian characters. It must be inferred, therefore, that the evolutionary development of a human limb structure occurred at an even earlier time, and well in advance of corresponding changes in the brain, skull and dentition. It may be noted that some of the features of the skeleton of Neanderthal Man have been assumed to represent to some extent a transitional stage between *Homo sapiens* and a "gorilloid" type of ancestor. But the evidence now available from the much more ancient remains of *Pithecanthropus* indicates quite definitely that such "simian" features as may be found in the Neanderthal skeleton are the result of secondary retrogressive changes.

Let us now turn our attention to the evidence of the dentition in the consideration of human phylogeny. There is quite sound evidence that the relatively small and brachydont canine tooth of *Homo sapiens* is the result of an evolutionary retrogression from a larger and more powerful tooth. This is shown by the fact that in modern Man, although the canine has no specialised function, it is provided with an unusually long root, its eruption is retarded till after that of the premolar teeth, and in some individuals it is pointed and projects well beyond the level of the crowns of the adjacent teeth. Moreover, in some of the extinct primitive hominids, particularly *Pithecanthropus*, the canine teeth were rather more massive than in *Homo sapiens* and showed certain moderately simian features. On the other hand, it seems improbable that in human ancestry the canines were ever as extremely developed as in the modern large apes, for this degree of specialisation inevitably leads to secondary

specialised changes in adjacent teeth, as well as in the general architecture of the skull. For example, the first lower premolar tooth takes on a sectorial form in order to provide an adequate functional opposition to the upper canine in occlusion. The dental arcade, also, becomes disposed in an elongated U-shape, with the premolar and molar teeth forming almost straight parallel rows, terminating abruptly anteriorly in the enlarged tusk-like canines. In Man, the dental arcade is more evenly curved in parabolic form, and the first lower premolar preserves a primitive bicuspid character. Thus, as with the limb structure, there is reason to believe that some of the typical features of the dentition in the Pongidæ represent aberrant specialisations, which make it improbable that they could have found a place in the evolutionary development of a hominid type of dentition. It is true, as has often been pointed out, that the dentition of the modern anthropoid ape shows considerable variation, that, for example, in female gorillas the canine may be relatively reduced, and in some chimpanzees the sectorial form of the first lower premolar tends towards a bicuspid form. But these partial modifications do not lessen the fact that in the Pongidæ there is a prevailing tendency towards specialisation in the characters mentioned above, and that this type of specialisation has evidently been avoided in the Hominidæ.

The general thesis that Man is derived from ancestral forms not very dissimilar in their main structure from the chimpanzee has appeared to gain support from the palæontological evidence of late Miocene and early Pliocene apes. Many jaws and teeth of these fossil apes have been recovered in Europe, Asia and Africa, and most of them have been assigned to the genus *Dryopithecus*. In several features of the dentition, the dryopithecine apes were more generalised than the modern apes, and in some species there are certain resemblances to Man in the proportions of the lower molar teeth and in the fact that the canines are not very highly specialised. Other species in their molar pattern suggest an approximation to the gorilla, chimpanzee or orang. Thus the opinion has gained ground that they represent an ancestral group which gave rise by divergent evolution to all the existing large Hominoidea, that is to the modern large apes and also to Man. This view has been particularly developed by the American authority, Dr. W. K. Gregory, in a series of outstanding monographs on the dentition of the primates. Gregory has recognised a distinctive pattern of cusps in the lower molars of *Dryopithecus*, which he calls the "*Dryopithecus* pattern," and from which he believes the cusp pattern characteristic of human molars has been derived. In the "*Dryopithecus* pattern" the

hypoconid has a wide contact with the metaconid, so that the sulci separating all the cusps are arranged to form a somewhat complicated double-Y pattern. In the evolution of the human molars, the progressive enlargement of the entoconid has gradually obliterated the contact between the hypoconid and metaconid to produce a simple cruciform pattern of sulci. But with the accession during recent years of more fossil ape material the question arises whether the term "*Dryopithecus* pattern" has not become somewhat misleading, for the same pattern is also found in other extinct genera such as *Sivapithecus*, *Ramapithecus*, *Proconsul* and *Xenopithecus*. Indeed, it now seems that this particular pattern may have been characteristic of all the primitive Hominoidea, and it can no longer be argued, therefore, that the human type of molar has any closer morphological affinities with that of *Dryopithecus* rather than with any other of the extinct and more generalised hominoids. The fact is that, although the dentition of the Dryopithecinæ shows certain generalised features, it had already developed some of the specialised characters which are distinctive of the modern Pongidæ. For example, it shows the parallel arrangement of the premolar-molar series ending anteriorly at an enlarged and tusk-like canine, and the first lower premolar tooth is modified to some extent as in modern apes.* In so far as these are specialisations which have apparently been avoided in the Hominidæ, it seems probable that the latter must have been derived from a group of early hominoids which were more generalized than the genus *Dryopithecus*.

It will be clear that the line of reasoning which we have so far followed can only lead to the establishment of *probabilities*. The evidence of pure comparative anatomy and embryology in its relation to evolutionary problems is, of course, only indirect, and it can do no more than give us a hypothetical picture of the sequence of events which seems most likely to have occurred in any particular line of evolution. Such conjectures can only be confirmed (or may perhaps be rejected) by the concrete and direct evidence provided by palæontological data. It is in this connection, indeed, that the fossil remains of the Australopithecinæ are of paramount importance for the consideration of human phylogenesis. As we shall see, they do tend in a rather remarkable way to favour the tentative conclusions, already outlined on the basis of the indirect evidence, that the line of human evolution probably did not pass through a phase

* This seems to have been the case even in the Siwalik species *Ramapithecus brevirostris*, which, in certain respects, is said to show some remarkable human characters in the disposition of its dental arcade (Gregory, Hellman and Lewis, 1938).

marked by adaptations to brachiating habits and by the dental specialisations found in the modern large apes.

The Anatomy of the Australopithecinæ *

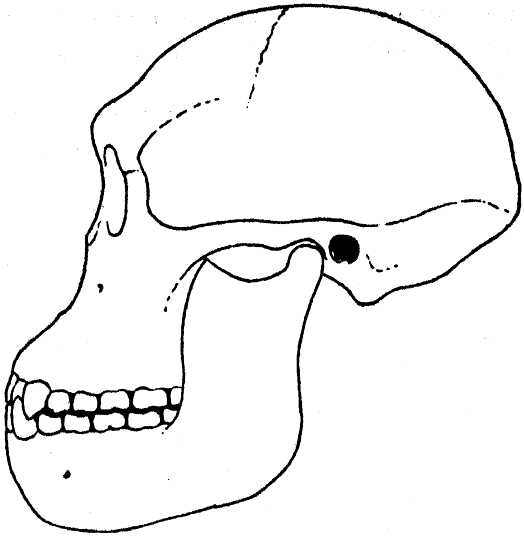
It is unnecessary in this communication to give a systematic description of the anatomy of the Australopithecinæ, for this has already been done in numerous papers by Dart and Broom (for references see the extensive bibliography at the end of the recent monograph by Broom and Schepers, 1946). A detailed report of the personal observations made by the present writer is also in course of publication. However, the essential features presented by the fossil material can be quite briefly enumerated.

The brains of these extinct hominoids were comparable in size with those of the modern large anthropoid apes. That of the immature *Australopithecus* is estimated to have been about 500 c.c. (probably increasing to almost 600 c.c. in the adult male), and that of the young adult *Plesianthropus* type specimen about 450 c.c. In so far as it is possible to conjecture the body size by reference to the limb bone fragments, it may be inferred that the size of the brain in relation to the body weight was probably rather larger than in the chimpanzee or gorilla, but it definitely falls within the simian range. On the other hand, the jaws were massive. Thus in its *general* proportions, the Australopithecine skull has a superficial appearance not unlike that of a chimpanzee, but in the details of its construction it actually presents many differences which are most conveniently tabulated as follows:

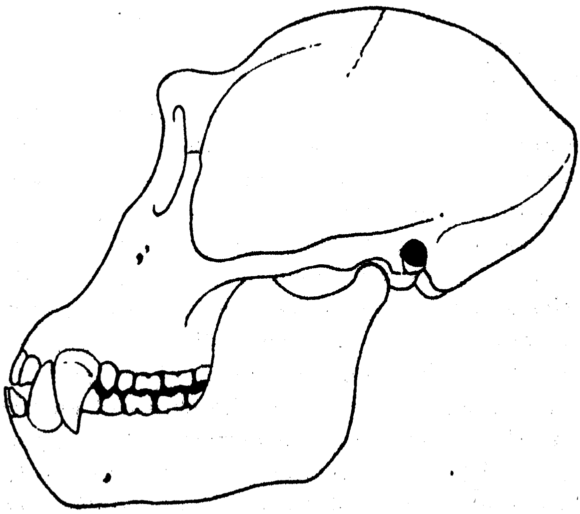
(1) The muscular ridges which are commonly so conspicuous in the modern large apes are much less strongly developed. This applies particularly to the temporal ridges, of which there is no sign in the type *Plesianthropus* skull for a distance of at least 33 mm. from the mid-line (although the third molar teeth had already erupted). A comparative study of the skulls of chimpanzees and gorillas shows that at this stage of maturity the temporal ridges of either side have either fused or they are quite close to the mid-line. The supraoccipital portion of the type *Plesianthropus* skull also makes it clear that powerful nuchal crests were lacking in this region.

(2) The type *Plesianthropus* skull shows clearly that the upper part of the coronal suture and the anterior half of the sagittal suture were still completely patent. In the recent apes, the sutures of the cranial vault close very early, commencing at the time of the erup-

* For illustrations of the Australopithecine fossil material, the reader is referred to the monograph by Broom and Schepers (1946), and to a paper by the present writer which will shortly appear in the *Journal of Anatomy*.



(a)



(b)

Fig 1.—Above (a) is shown a drawing of a tentative reconstruction of a young adult skull of *Plesianthropus*, based primarily on the type specimen of this Australopithecine genus. It corresponds closely with a similar reconstruction by Dr. Broom, except for slight modifications in the supra-orbital and occipital regions. The contour of the supra-orbital region is based on a consideration of the relationship of the endocranial cast to the glabella and the base of the skull, and that of the occipital region on the endocranial cast and the portion of the supra-occipital bone which has been preserved. A comparison with the drawing of

tion of the second molar tooth (Krogman, 1930). The still patent sutures in *Plesianthropus* suggest a more prolonged growth period in the Australopithecinæ than is found in the modern large apes.

(3) The *Australopithecus* skull has a true spheno-parietal contact which is but rarely found in the African anthropoid apes of to-day. (Neither in *Plesianthropus* nor in *Paranthropus* can the sutural pattern in the region of the pterion be deciphered in the material available at the time of writing.)

(4) The relation of the frontal pole of the brain to the glabella and nasion resembles the human rather than the simian condition. The details of the supra-orbital region of the skull of *Australopithecus* are quite unlike those of the recent large apes (at *any* stage of growth), and bear a remarkable resemblance to those of *Homo*. There is no sign in this immature skull of an incipient supra-orbital torus such as is found at the same relative stage of development in those anthropoid apes which have a strong torus in the adult skull.

(5) The contour and orientation of the zygomatic bone show detailed resemblances to *Homo*, and the lack of a simian torus zygomaticus on the temporal surface of the bone also seems very significant.

(6) The contour of the maxilla shows certain resemblances to that of Man, and the infra-orbital foramen in all three Australopithecine genera appears to be single (and not multiple as in recent apes).*

(7) The "hollowed-out" character of the glenoid fossa, bounded

* Reference should perhaps be made to the question of the facial portion of the premaxilla, for the groundless assumption has been made that the suppression of this portion in the human skull must be a character of great phylogenetic antiquity. However, there is no valid evidence in support of its supposed antiquity and there is no reason to suppose that its disappearance may not have been relatively recent (in the geological sense). Actually, the present writer was unable to detect with certainty the facial part of the premaxillary suture in the *Plesianthropus* maxillæ which he examined, and the possible traces of its upper part in the *Australopithecus* skull also seem to be rather dubious. But even if the facial portion of the premaxilla were present in the make-up of the Australopithecine skull, this cannot be used

chimpanzee (*b*) shows some of the outstanding features in which the Australopithecine skull makes a closer approach to the Hominidæ. These include a less-pronounced development of the supra-orbital ridges, a higher position of the zygomatic arch relative to the floor of the orbit, a less extensive development of the temporal fossa and the nuchal crest, less-pronounced alveolar prognathism, smaller incisors and canine teeth, and a relatively more forward position of the external auditory meatus and the occipital condyles. Note, also, that the brain case is set higher in relation to the upper part of the face than in the chimpanzee. Both the skulls are shown at two-fifths their natural size.

anteriorly by a transversely disposed articular eminence, approximates to the human condition. The post-glenoid process, which is so powerfully developed in modern apes, is represented in *Paranthropus* by quite a small tubercle of remarkably human appearance, and the tympanic bone is well exposed below the process and presents a flattened anterior surface which forms throughout the whole of its extent (as in Man) the posterior wall of the glenoid fossa.

(8) The mandible (as known from that of *Paranthropus*) is massive, but the contour of its body is human rather than simian. Indeed, the horizontal curve of the outer surface of the body (approximately mid-way between the alveolar and lower borders) coincides to a remarkable degree with that of the Heidelberg mandible.

(9) The foramen magnum is situated relatively further forwards on the base of the skull than in the modern large apes. This statement is based on objective evidence from the skull material of all three Australopithecine genera, and the evidence is consistent. It is further confirmed by the forward slope of the terminal part of the sigmoid sinus as shown on the endocranial casts. This forward slope is conditioned by the forward displacement of the jugular foramen which, again, is related to the position of the foramen magnum.

The Teeth of the Australopithecinæ.—The dentition of the Australopithecinæ is so remarkably human in most of its characters that there can be little doubt that, if the teeth alone had been discovered, they would have been referred to the Hominidæ. They have been studied in great detail by a number of experienced authorities, and the conclusion of the latter may be briefly summarised. Dart (1934) concluded that there is no really significant feature in the dentition of *Australopithecus* that can be termed simian. Broom (Broom and Schepers, 1946) sums up his comprehensive survey of all the (then) available Australopithecine teeth by saying that "the dentition of both the milk and the permanent sets agrees remarkably closely with the dentition of Man, and only differs in retaining a few more primitive characters and in being a little larger in most cases." Gregory (1930), in a comparative study of the teeth of *Australopithecus*, drew up a list of resemblances to or differences from other hominoids; out of 26 characters he found

as a serious argument against possible affinities with the progenitors of the Hominidæ. The remarkable suggestion that the suppression of the facial part of the premaxilla in the human skull precludes the idea of any close relationship between Man and the modern anthropoid apes might be paralleled by a similar inference that the suppression of elements in the tail precludes any possibility of a close relationship between manx cats and cats with ordinary tails!

that in 20 the teeth are transitional to, or nearer to, primitive Man, while in only three characters are they nearer to the chimpanzee or gorilla. In a subsequent intensive study of all the Australopithecine teeth then available, Gregory and Hellman (1939) were led to agree with Broom that " in South Africa there once lived apes which had almost become men." Abel (1931) argued that there were some indications of specialisation in the dentition of *Australopithecus*, but he recognised the remarkable hominid features, such as the fact that little difference is to be found between the first milk molar and that of Man. Adloff (1932) concluded from his comparative studies that the teeth of *Australopithecus* should by definition be regarded as human teeth. Senyürek (1941) gave as his opinion that the teeth of the Australopithecinæ are nearer to the primitive hominids than to the apes, an opinion which had previously been also expressed by Montandon (1939). The present writer, from his personal studies of the original fossil material, can affirm the astonishingly human characteristics of the Australopithecine dentition, emphasising particularly the parabolic contour of the dental arcade, the disposition and relatively small size of the permanent canine teeth, the human appearance of the premolar teeth (particularly the anterior lower premolars as seen in *Paranthropus*), the type of wear shown in all the premolar and molar teeth, the diminutive size of the milk canine (particularly in the immature *Paranthropus* jaw discovered by Dr. Broom only a few feet from the spot where the adult skull was found at Kromdraai), and the human appearance of the first milk molars. Another point to which attention may be drawn is the *degree* of attrition with exposure of the dentine, shown in the milk molars of *Australopithecus*, in spite of the fact that the first permanent molars had not completed their eruption. This perhaps suggests that the interval between the eruption of the milk molars and the first permanent molar may have been as prolonged as it is in Man. Again, the degree of *differential* attrition in the three lower molars of the adult *Paranthropus* jaw is very striking. In this specimen the last molar had only recently come into position, for it is practically unworn. Yet the first molar is already planed down to an approximately flat surface with exposure of the dentine, while in the second molar the minor sulci and crenations have disappeared and the main cusps are worn smooth. Such a degree of differential attrition is rarely if ever found in the anthropoid apes at a corresponding stage of growth. But it is not uncommon in Man (particularly in primitive races living on a coarse diet) and is presumably here related to the much longer interval between the eruptions of the molar teeth in the

human dentition. The degree of attrition of the upper premolar teeth in the *Plesianthropus* type specimen, relative to that of the second upper molar tooth, is also instructive, suggesting that the former must have erupted some time before the latter as in Man, and not subsequently as in the anthropoid apes. Thus, this evidence of attrition, though not conclusive, does lead to the inference that in the sequence of the appearance of the permanent teeth, as well as in the length of the intervals between their eruption, the Australopithecinæ probably resembled Man and not the recent large apes.

The Limb Bones of the Australopithecinæ.—The limb bone material discovered by Dr. Broom at Kromdraai and Sterkfontein and ascribed by him to *Paranthropus* and *Plesianthropus* is of unusual interest, mainly because of the hominid features which it presents. Indeed, the combination of limb bones so human in many of their anatomical details with a brain development scarcely exceeding that of the gorilla or chimpanzee (so far as this can be determined from endocranial casts) must inevitably raise the question whether the limb bones are correctly to be associated with the fossil remains of the skulls. However, there seems to be no reasonable doubt that it is legitimate to do so. Within one foot of the type skull of *Paranthropus* and embedded in the same bone breccia were found the lower end of a right humerus, the upper end of a right ulna and a right talus (astragalus). The humeral and ulnar fragments articulate in close conformity with each other, and thus almost certainly represent the component parts of the right elbow joint of the same individual. At Sterkfontein a right capitate bone and the lower end of a left femur have been so far discovered. These were not found in direct association with the remains of the skull and teeth of *Plesianthropus*, but they were derived from the limestone matrix at the site where the remains of not less than eight separate skulls of *Plesianthropus* have been discovered. All these bones are identifiable as those of large hominoids, and no other remains of any large hominoid have been found at the sites apart from the skulls of *Paranthropus* and *Plesianthropus*. Also, no other remains of limb bones have been discovered at either site which could possibly be attributed to these two genera. Lastly, in spite of an extensive search through great quantities of breccia, during which many skulls, teeth and limb bones of lower mammals have been found, no trace has been seen of human skulls and teeth, nor any signs of human habitation. The intrinsic evidence of the limb bones themselves provides the final justification for their association with *Paranthropus* and *Plesianthropus*, for some of them show a remarkable combination

of simian and human features which is obviously in harmony with the similar sort of combination shown by the skull, teeth and brain of the Australopithecinæ.* The main points about this limb bone material are as follows:

(1) The humerus and ulna fragments of *Paranthropus* lack the powerful muscular ridges found in the brachiating apes, and appear to be quite closely similar to those of *Homo sapiens*. A possible exception is the relative position of the trochlea. In the human (and more so in the simian) humerus, the trochlea is set well forward in relation to the shaft and to the medial epicondyle. In *Paranthropus* the transverse central axis of the trochlea lies approximately within the line of the long axis of the lower end of the shaft of the humerus. The significance of this unusual alignment is not clear.

(2) The talus of *Paranthropus* is a very small bone. Its superior articular facet resembles that of Man in being relatively broad and also in its even curvature from side to side. The lateral fibular facet is less strongly curved and less extensive than in recent anthropoid apes. The medial tibial facet is quite similar in contour and extent to that of Man and its articular surface is approximately vertical. In the gorilla and chimpanzee this surface slopes medially to a marked extent and in the chimpanzee it is excavated anteriorly to form a cup-shaped socket. While the main body of the talus is thus human rather than simian in its morphological features, the "head" of the bone is remarkable for the wide extent of its articular surface in relation to the size of the bone as a whole. Medially the navicular surface projects to a distance of 8 mm. beyond the level of the plane of the medial tibial articular facet, *i.e.* considerably further relatively than in a modern human talus. It is suggested that, whereas the body of the talus is constructed for stability in weight bearing in a standing position, the broad curvature of the head of the bone is related to a greater mobility of the fore part of the foot than is possible in Man, presumably allowing for the transference of a major component of the body weight directly forwards as in Man, but also providing for its deflection medially to an extent which is found in the modern anthropoid apes with their divergent great toes. It may have been, therefore, that in *Paranthropus* the

* One other point may be mentioned in this connection. The *general* simian proportions of the brain and skull might lead to the expectation that the limb bones would show all those simian characteristics which are directly related to an arboreal life and brachiating habits. But the climatological evidence indicates almost certainly that the Australopithecinæ lived not in a forest environment like the modern anthropoid apes, but in rather arid and they must, therefore, have been well adapted for terrestrial

hallux was capable of some degree of divergence which would allow of its use for grasping purposes.

(3) The capitate bone of *Plesianthropus* is also a very small bone. It is human in its general proportions, in the contour of its articular facet for the third metacarpal bone, and in the position and orientation of the facet for the second metacarpal, but simian in the fact that a considerable part of the lateral aspect of the bone is taken up by a ligamentous surface hollowed out to form a marked concavity, and by the development of a pronounced tubercle (presumably also for the attachment of ligaments) at the distal end of the palmar aspect. It may perhaps be inferred that in *Plesianthropus* the movements between the capitate and adjacent bones were not so free as in modern Man and that the hand was to that extent less plastic.

(4) The lower end of the femur of *Plesianthropus*, if considered entirely isolated from the circumstances of its discovery, would probably be referred by most anatomists to *Homo sapiens*. It is a very small bone (and thus harmonizes with all the other limb bones also ascribed to the Australopithecinæ), but relatively robust. The obliquity of the shaft (*i.e.* the angle between the axis of the shaft and the vertical axis in the standing position) contrasts strongly with that of the femur of modern large apes, and comes well within the human range. The patellar surface, also, is not broad and shallow as in the apes; it is relatively deeper, and laterally slopes rather abruptly into a prominent lip as in Man. The shape, disposition and proportionate sizes of the condyles, again, appear to be typically human. However, the intercondylar notch is prolonged forwards to an unusual extent, in association with an exaggerated impression related to the anterior cruciate ligament, and it has not been possible, so far, to match this curious feature in modern human races. The important inference to be drawn from a comparative study of the femur is that its owner must have been capable of standing and walking in the erect position somewhat as modern Man does. It is interesting to note that this is in conformity with the position and orientation of the foramen magnum in the base of the skull, and, indeed, had already been anticipated by Dart from a consideration of these features.

The Relationship of the Australopithecinæ to the Hominidæ

If the limb bones discovered at Sterkfontein and Kromdraai belong to *Plesianthropus* and *Paranthropus* (and reasons have been adduced above for accepting this association as valid), we are in a position to construct provisionally a fairly complete picture of the

Australopithecinæ by reference to their fossil remains (now by no means inconsiderable in quantity). They were hominoids of small stature (probably similar in this respect to the pygmy races of present-day mankind), with brains not much larger relatively than those of the gorilla and chimpanzee, massive jaws showing many human features, a dentition fundamentally of human type (except for the large size of the permanent molars and premolars) and lacking the tusk-like canines and the large incisors of the modern anthropoid apes, and limbs approximating in their structure and proportions to those of the Hominidæ. They were evidently capable of standing and walking with an almost erect posture, and the hands and feet were relatively small and delicately built. Now it can hardly be doubted that, by the usual morphological criteria, this extinct subfamily, with its many remarkable human characters, must be assigned to a zoological position much closer to the Hominidæ than are the modern large apes. This, at least, is the firm conclusion which has been unanimously reached by all those palæontologists who have so far made a detailed comparative study of the Australopithecine material. But, from the point of view of our present discussion, the importance of the Australopithecinæ lies in the fact that they represent a level of evolutionary development (so far as the size of the brain is concerned) which corresponds with that of the modern large apes, without at the same time showing the characteristic specialisations of the latter in the skulls, dentition and limbs. Thus there seems no longer to be any good reason for postulating an anthropoid ape phase immediately preceding the hominid phase of human evolution, in which such specialisations were manifested, and the evidence becomes stronger for the inference that the line of evolution leading to Man probably diverged from that leading to the modern large apes before these specialisations were developed at all. The other important point which is made clear by these South African fossils is that large hominoids once existed in which brains of simian proportions were combined with limbs which had already reached an evolutionary stage approximating to that of Man. This suggests strongly that the point of divergence of the human line of evolutionary development must be assigned to a geological date considerably earlier than many palæontologists have hitherto been prepared to accept. The question now arises whether the Australopithecine fossils so far discovered are likely to bear any direct or indirect ancestral relationship to *Homo*. A careful analysis of all the purely morphological data brings to light no serious grounds for precluding such a possibility. Indeed, it is possible to go further and affirm that the morphological characters of the Australopithecinæ conform

quite closely to theoretical postulates for an intermediate stage of human evolution, which had been based on the indirect evidence of comparative anatomy. But the place occupied by the Australopithecinæ in human phylogenesis will be precisely determined only when more adequate palæontological and geological data are available. According to Broom's tentative estimate (1946), the Sterkfontein deposits are of upper Pliocene date (or earlier) and the Taungs deposits may even be attributed to the middle Pliocene. If it should be established, as the results of further systematic excavations, that the Australopithecine fossil material is no older than the early Pleistocene or late Pliocene, it must probably be assumed that, at the most, these extinct hominoids represent the little modified survivors of the ancestral stock from which, at a still earlier date, the line of human evolution originated.

Future research is certain to provide the data on the basis of which the systematic position of the Australopithecine fossils will be finally established. With all the information already available, however, it seems quite clear that they represent one of the most outstanding discoveries in the field of human palæontology, and there can be no doubt that they are of fundamental importance for the consideration of problems of human evolution.

ADDENDUM

Since this paper was written, some details of Dr. Broom's new discoveries have come to hand. The most important of these discoveries is the almost complete skull of an old individual (*Plesianthropus*) from Sterkfontein (see *Nature*, May 17, 1947). Among the outstanding characters of this skull are the contour of the brain-case (particularly in the frontal and occipital regions) and its orientation in relation to the facial skeleton. In these respects the new skull reproduces and confirms the features represented in the reconstruction of the young adult *Plesianthropus* skull (see Fig. 1 (*a*) in this paper). Other noteworthy features clearly demonstrated by the new skull are the position of the foramen magnum and the degree of flexion of the basi-cranial axis at the prosphenion.

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BIOLOGICAL METHYLATION

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The importance of the methyl group in organic and biochemistry is apparent even from a very superficial consideration of some of the commonest natural products. Thus, trimethylamine occurs in the blossom of the common hawthorn, *Cratægus oxyacantha*, and also in herring-brine, where it probably arises by bacterial reduction of trimethylamine oxide, which is an ingredient of the tissues of many fish and of crab and lobster muscle [1]. The corresponding quaternary ammonium base, tetramethylammonium hydroxide $(CH_3)_4N.OH$, is elaborated by the sea-anemone, *Actinia equina* [2]. Owing to the well-known "curare effect" of this base, and of similar quaternary compounds, it has been suggested that the anemone may employ it in order to paralyse the smaller marine organisms on which it feeds. The presence of choline $(CH_3)_3\underset{OH}{\overset{N}{=}}.CH_2CH_2OH$ in plant and animal tissues is well-known. Recently a related compound betaine $(CH_3)_3\overset{+}{N}.CH_2.CO.\overset{-}{O}$ has been found in numerous marine animals [3]. Prior to this discovery its main interest had lain in its occurrence in sugar-beet.

Creatine $NH_2.C{:}(NH).N(CH_3)CH_2COOH$ found in the muscles of animals has received much attention from biochemists from many points of view, and especially as regards its relation to methionine $CH_3.S.CH_2CH_2CH(NH_2)COOH$. This amino-acid, isolated from protein by Mueller [4] and synthesised by Barger and Coyne [5], is steadily acquiring more and more importance. Its conversion to cystine in the body has recently been elucidated during the course of some brilliant work in America [6, 7]. Methionine is doubtless the precursor of the methylsulphone isothiocyanate cheirolin $CH_3SO_2CH_2CH_2CH_2N{:}C{:}S$ which occurs in the wall-flower [5, 8]. The occurrence of $>NCH_3$ groups in numerous alkaloids is well-known. In addition to these compounds, in which the methyl group is attached to nitrogen or sulphur, numerous natural products, such as vanillin, eugenol and anethole, contain methoxy groups. Allied to these are piperine and safrole containing the $CH_2{<}\begin{matrix}O—\\O—\end{matrix}$ grouping which may have the same origin as $—OCH_3$. Finally the terpenes, polyterpenes and sterols contain methyl groups linked to

carbon, including the interesting case of certain sterol derivatives, in which the attachment is "angular." In all the compounds mentioned the origin of the methyl group is of particular interest, and this question has given rise to much discussion and experimental work in recent years. In the case of $C—CH_3$ groupings the immediate origin may sometimes be different from that of $N—CH_3$ or $S—CH_3$.

The phenomena of biological methylation and the theories relating to its mechanism may best be presented by considering the historical development of two lines of investigation which have been pursued simultaneously and independently at the University of Leeds and at Cornell University in America. The first has dealt entirely with methylation processes in moulds, the second in animals.

A description of the work at Leeds, which began in 1931, may be prefaced by a brief account of some experiments carried out in Italy forty years earlier.

In 1891 B. Gosio [9] exposed a potato-mash, containing arsenious oxide, to the air. It quickly became infected with moulds and bacteria and evolved a garlic odour. Some of these organisms he isolated in pure culture. The bacteria produced no volatile odorous compound under these conditions, but some of the moulds were intensely active, especially one which Gosio named *Penicillium brevicaule*—the modern nomenclature is *Scopulariopsis brevicaulis.* Other organisms which exhibited this phenomenon were *Aspergillus glaucus*, *A. virens* and *Mucor Mucedo.* C. Thom and K. B. Raper [10] extended this list to include *A. fischeri*, *A. sydowi* and a few soil organisms. The author finds that a strain of *A. versicolor* should also be added to this list.

B. Gosio [9] then devised a method for the detection of traces of arsenic in various materials. An evaporated aqueous extract was added to a slice of sterile potato previously inoculated with *S. brevicaulis.* After a few hours at about 25–30° inorganic arsenic could be detected by the production of a garlic odour. Smith and Cameron [11] state that one-millionth of a gram of arsenious oxide in one gram of material can thus be recognised. The method is more sensitive than the Marsh test, but is not adaptable for quantitative work.

By passing the gas from arsenical cultures of *S. brevicaulis* through a hot tube, Gosio concluded that the gas contained an alkylarsine. P. Biginelli [12] aspirated "Gosio-gas" through mercuric chloride in dilute hydrochloric acid. The resulting precipitate was assigned the composition $(C_2H_5)_2AsH.2HgCl_2$ and Biginelli concluded that the gas was diethylarsine. Klason [13]

regarded it as diethylarsine oxide. Wigren [14] showed that the behaviour of these compounds towards acid mercuric chloride (Biginelli's solution) was different from that of Gosio-gas.

Owing to the uncertainty regarding the nature of Gosio gas, work was commenced by Challenger in 1931. Four strains of *Scopulariopsis brevicaulis* were employed.

Sterile aqueous solutions of various arsenic compounds were added to bread cultures of *S. brevicaulis* arranged in series. Sterile air was passed through and the volatile arsenic compound absorbed in Biginelli's solution. Using arsenious oxide (0·2–0·25 per cent. in the bread) two different deposits were obtained according to the concentration of the mercuric chloride, consisting of the dimercurichloride and monomercurichloride of trimethylarsine, $(CH_3)_3As.2HgCl_2$ and $(CH_3)_3As.HgCl_2$. Gosio-gas is therefore trimethylarsine [15]. Direct comparison with an authentic specimen confirmed this conclusion. With sodium methylarsonate $CH_3AsO(ONa)_2$ (1–1·5 per cent in the bread) or sodium cacodylate $(CH_3)_2AsO.ONa$ (0·1–0·3 per cent. in bread) (free from inorganic arsenic) the evolved gas gave the same mercurichloride.

The identity of Gosio-gas was then confirmed by several observations:

By absorption in nitric acid trimethylhydroxyarsoniumnitrate $(CH_3)_3As.(OH).NO_3$ and the corresponding picrate were prepared, identical with those obtained from the synthetic arsine.

Gosio-gas, with alcoholic benzyl chloride, gave a quaternary salt which with aqueous sodium picrate gave trimethylbenzylarsonium picrate $(CH_3)_3As.CH_2C_6H_5.OC_6H_2(NO_2)_3$.

The identification of Gosio-gas solved a problem which had interested chemists since the early days of the nineteenth century—the origin of the toxic effects which were observed in houses decorated with wall-paper containing arsenical pigments. The wall-paper in such rooms was usually damp and mouldy and a garlic odour was present. In one test case it was possible to exclude arsenical dust as the cause. Early suggestions that the toxic product was arsine, AsH_3, have received no confirmation. Arsine is certainly absent from the gas evolved by *S. brevicaulis* in pure cultures containing inorganic arsenic.

Summaries of the literature on the subject, which is very extensive, have been published by Abel and Buttenberg [16], Huss [17], and Maassen [18]. Later reviews dealing with biological methylation in its wider aspects have been compiled by the author [19].

These cases of arsenical poisoning have occurred at intervals

over the last century. As recently as 1931, before the identification of Gosio-gas, the deaths of two children in the Forest of Dean were reported. The parents and two other children were also affected. The death of one of the children was shown to be due to arsenical poisoning. The house was damp and ill-ventilated. Here it was shown that the arsenic arose from the coke-breeze in the wall-plaster. The outer wall was very damp, and the wall-paper, originally almost free from arsenic, became contaminated through infiltration while infected with moulds. Full details of the case are available (20).

Alkylarsonic Acids and *S. brevicaulis*

It seemed possible that in the experiments with sodium methylarsonate and cacodylate, the mould might have caused fission of the arsenic-carbon link, giving inorganic arsenic, or that the trimethylarsine might have arisen by reduction followed by dismutation thus :

$$CH_3AsO(OH)_2 \rightarrow CH_3As(OH)_2 \rightarrow CH_3AsO$$
$$3CH_3AsO = (CH_3)_3As + As_2O_3 \quad \text{and}$$
$$(CH_3)_2AsO.OH \rightarrow (CH_3)_2AsOH, \qquad 3(CH_3)_2As.OH = 2As(CH_3)_3 + As(OH)$$

A decision on this point was quickly reached, however. With sodium ethylarsonate in bread cultures of the mould dimethylethylarsine $(CH_3)_2AsC_2H_5$ was evolved and identified as the mercurichloride, thus eliminating both these possibilities. Absorption in benzyl chloride yielded ethyldimethylbenzylarsonium chloride, and in nitric acid ethyldimethylhydroxyarsonium nitrate, which were characterised as the picrates. This reaction was then studied further [21]. Addition of (*a*) diethylarsonic acid $(C_2H_5)_2AsO.OH$, (*b*) *n*-propylarsonic acid and (*c*) allylarsonic acid $CH_2{:}CH.CH_2AsO(OH)_2$, to similar cultures of the same strain of the mould in concentrations varying from 0·2 to 0·5 per cent. gave mixed methylated arsines.

From (*a*) methyldiethylarsine was obtained and from (*b*) dimethyl-*n*-propylarsine. This arsine was also obtained with methyl-*n*-propylarsonic acid and *S. brevicaulis*. It was identified as the dimercurichloride and as dimethyl-*n*-propylhydroxyarsonium picrate. Ethyl-*n*-propylarsonic acid gave methylethyl-*n*-propylarsine and (*c*) gave dimethyallylarsine $(CH_3)_2As.CH_2CH{:}CH_2$ characterised as the dimercurichloride and as benzyldimethylallylarsonium picrate. These compounds were identical with authentic specimens.

Later work by the Leeds school has shown that a few moulds such as *Aspergillus niger*, *Penicillium notatum* and *Penicillium*

chrysogenum, while incapable of producing trimethylarsine from inorganic arsenic, will readily convert alkylarsonic acids $RAsO_3H_2$ and $R.R'AsO.OH$ to alkylmethylarsines $R\,As(CH_3)_2$ and $RR'AsCH_3$. Further instances of the methylating powers of these organisms will be discussed later.

The moulds which have been shown to possess this methylating action must not be confused with certain organisms which are "arsenic tolerant" but are unable to produce methyl-derivatives of arsenic. Moulds have been found growing in solutions of potassium arsenite containing only the barest traces of organic matter. The literature has been summarised by the author [22].

Methylation of Inorganic Compounds of Other Elements

O. Rosenheim [23] showed that, when *S. brevicaulis* was grown upon sterile bread containing inorganic compounds of selenium and tellurium, unpleasant odours were evolved. The substances responsible were not identified. A. Maassen [24], judging entirely from odour, stated that the volatile products were diethyl selenide and diethyl telluride. He also examined the breath of animals injected with inorganic selenites and tellurites, and believed that here the odour was due to dimethyl selenide and dimethyl telluride. Maassen concluded, therefore, that the animal body deals differently with compounds of selenium and tellurium than does the organism of the mould.

Methylation of Inorganic Compounds of Selenium

The gas evolved from Rosenheim's cultures containing selenium compounds was identified by F. Challenger and H. E. North [25]. The volatile products from several cultures of two different strains of *S. brevicaulis* on bread containing sodium selenate or selenite were aspirated through absorbents and characterised as dimethyl selenide mercurichloride and mercuribromide $(CH_3)_2Se,HgX_2$, dimethylhydroxyselenonium nitrate $(CH_3)_2Se(OH)NO_3$, dimethyl selenide α-platinochloride, and dimethylbenzylselenonium chloride $(CH_3)_2Se(CH_2C_6H_5)Cl$, isolated as the picrate.

Methylation of Inorganic Compounds of Tellurium

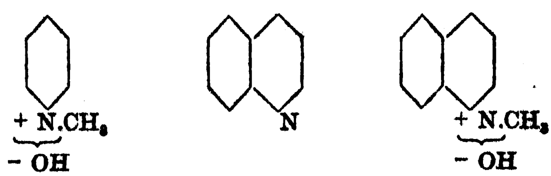
The odour exhaled by animals receiving inorganic derivatives of tellurium was first observed in 1824. Later on A. Hansen [26], on administration of potassium tellurite to dogs or men, detected a garlic odour in the breath after a few minutes. This lasted for

weeks and the persons in question were obliged to forsake the society of their fellows. During a recent investigation of inorganic derivatives of tellurium in Leeds, the odour could easily be detected in the vicinity of those engaged in the work, although they had never come into contact with organic compounds of tellurium. See also W. Blyth [27], who mentions the phenomenon of "bismuth breath", formerly well known to pharmacists and due to the presence of traces of tellurium in medicinal preparations of bismuth. Further details are given by G. Brownen [28], E. A. Letts [29], and A. Reissert [30]. In no case was the odorous substance satisfactorily identified, though the presence of hydrogen selenide or telluride was suggested.

(Miss) M. L. Bird and F. Challenger [31] aspirated the gases evolved from test-tube cultures of *S. brevicaulis* on bread containing potassium tellurite through only 5 c.c. of reagent in order to diminish oxidation of the volatile product. Dimethyl telluride mercurichloride was obtained and converted to dimethyl telluride dibromide. Absorption in alcoholic iodine gave dimethyl telluride di-iodide.

The mould gas is, therefore, dimethyl telluride, and Maassen's statement that it consists of the diethyl compound is incorrect. This conclusion was also confirmed with liquid cultures on 2 per cent. glucose-Czapek-Dox medium.

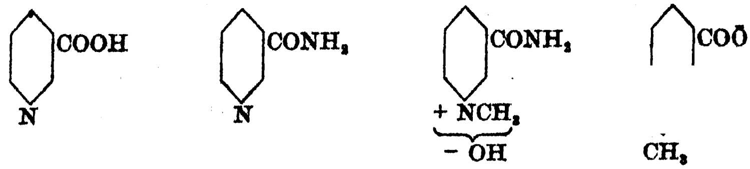
On the other hand, no rigid proof exists that the odour resembling an alkyl telluride, which is exhaled by men and animals in receipt of tellurite, is actually dimethyl telluride. Neither here, nor in the case of the analogous selenium odour, have sufficiently careful animal experiments been carried out. Bearing in mind, however, several well-established instances of biological methylation effected by animals, no reasonable doubt can remain. These cases, which have long been known, may now be summarised. Pyridine (I) and quinoline (III) are readily converted by dogs and other animals to the corresponding methylpyridinium (II) and methylquinolinium hydroxides (IV). [32, 33, 34].



(I) (II) (III) (IV)

Nicotinic acid (V) or its amide (VI) is converted in man or rats to N′-methylnicotinamide (VII). [35, 36]. Some trigonelline (VIII), an

ingredient of fenugreek (*Trigonellum foenumgraecum*), is also formed and was for many years believed to be the chief product [37].



(V) (VI) (VII) (VIII)

Owing to the presence of nicotinamide in the vitamin B complex and in co-enzymes, the methylation of the nitrogen atom of the pyridine nucleus has acquired an interest which was never expected at the time of the early work of His and of Ackermann.

Arsenic in the Animal Body

Owing to the similar behaviour of arsenic, selenium and tellurium in mould cultures, it would appear that arsenic also should be methylated in the animal body and exhaled as trimethylarsine. That no odour comparable in intensity with that produced by tellurite follows administration of medicinal doses of inorganic compounds of arsenic is well known [30], but occasional references to the presence of a garlic odour in the perspiration following upon arsenical poisoning occur [27].

Pleschtizer and Preobrajensky [38] passed the breath from patients in receipt of inorganic arsenic through bromine water. Treatment with ammonia and evaporation gave a slight residue, in which the presence of arsenic was detected by addition to cultures of *S. brevicaulis*, the garlic odour of "Gosio-gas" being obtained. The presence of some volatile compound of arsenic in the breath was thus rendered extremely probable, but the quantity was too small for identification. These authors, at that time unaware of the identification of Gosiŏ-gas as trimethylarsine merely quote Biginelli's statement [12] that it consists of diethylarsine.

Various authors (for references see [31]) mention the production of a garlic odour in the breath after ingestion or injection of cacodylic acid or its sodium salt. Bloemendal [39] passed the exhaled air of a rabbit, which had received 20 mg. of sodium cacodylate, through alkaline potassium permanganate solution, which then contained arsenic. The volatile product was not identified. From the behaviour of sodium cacodylate in cultures of *S. brevicaulis* the formation of trimethylarsine would be expected by reduction and further methylation. However, methylation does not occur readily in animals receiving arsenious oxide (see above), and trimethylarsine,

if formed from cacodylic acid in the animal body, might conceivably arise by dismutation, see p. 399.

Puntoni [40] attributed the garlic odour after oral administration of cacodylate to the effect of intestinal organisms, some of which he cultivated on cacodylate media, obtaining a similar odour. Using strains of the same and two other bacteria, Challenger and Miss Higginbottom [41] were unable to detect any odour in media containing arsenious oxide, sodium arsenate, sodium methylarsonate or sodium cacodylate, even after repeated cultivation on a cacodylate medium.

From the results just summarised it is clear that the question of the exhalation and possible methylation of arsenic by the animal body deserves further attention. It is possible that animals may be able to methylate organic derivatives of arsenic much more readily than arsenious oxide, in analogy with the behaviour of certain green *Penicillia*, see below.

Methylating Capacities of Other Moulds

A green mould which appeared in the Leeds laboratories as a spontaneous infection on bread-crumbs moistened with a tellurite solution was found by Dr. Thom of the U.S. Department of Agriculture, Washington, to be closely allied to *Penicillium notatum*, Westling. Cultures on bread and on 2 per cent. glucose-Czapek-Dox medium containing tellurite evolved dimethyl telluride, which was identified as before and as benzyldimethyltelluronium picrate.

P. chrysogenum Thom in tellurite-bread cultures gave dimethyl telluride, but only a faint odour was observed with *P. notatum*. Both organisms readily gave dimethyl selenide in bread cultures containing selenite or selenate. This was also produced in bread-selenate cultures by the " green mould ".

In bread cultures, none of the three green *Penicillia* gave trimethylarsine with arsenious acid, but all convert sodium methylarsonate to trimethylarsine, which is also produced in similar cultures of *P. chrysogenum* and *P. notatum* containing sodium cacodylate. Although methyl groups are present in the substrate, dismutation appears to be excluded, because bread cultures of *P. chrysogenum* convert sodium allylarsonate to allyldimethylarsine $CH_2{:}CH.CH_2As(CH_3)_2$.

Two strains of *Aspergillus niger* convert sodium methylarsonate and sodium cacodylate $(CH_3)_2AsO.ONa$ to trimethylarsine ; one of them also formed ethyldimethylarsine $C_2H_5As(CH_3)_2$ from ethylarsonic acid, and the other methylethyl-*n*-propyl arsine from ethyl-*n*-propylarsonic acid. Neither was able to methylate arsenious

acid. The reason for the selective action observed with the green *Penicillia* and with *A. niger* is under investigation.

FISSION OF THE DISULPHIDE LINK IN DIALKYL DISULPHIDES BY *S. BREVICAULIS* AND METHYLATION OF THE ALKYL-S GROUP

Following the experiments with arsenic, selenium and tellurium, attempts were made to produce dimethyl sulphide by the use of two different strains of *S. brevicaulis*. Negative results were obtained by Challenger and North [25] in bread cultures with sulphur, sodium sulphite, hydrogen sulphide solution, sodium thiosulphate, sodium tetrathionate, thiourea, thiodiglycollic acid and its sodium salt, sodium formaldehyde-sulphoxylate ("rongalite"), and also with sodium ethanesulphonate $C_2H_5SO_2.ONa$, and ethanesulphinate $C_2H_5SO.ONa$, the last-named compound in liquid cultures.

This was unexpected, since Pohl [42] noticed a leek-like odour in the breath of animals receiving injections of thiourea. The odorous product was non-reactive to sodium hydroxide or mercuric cyanide, and was therefore not an alkylthiol. It was absorbed by sulphuric acid and gave a precipitate with mercuric chloride. Pohl, therefore, concluded that the product was an alkyl sulphide. A similar odour is exhaled by patients suffering from hyperthyroidism and receiving thiourea [43, 44].

C. Neuberg and P. Grosser [45] stated that the precursor of the diethyl sulphide which was shown by J. J. Abel [46] to be evolved on warming the urine of dogs with alkali is methyldiethylsulphonium hydroxide; also that administration of diethyl sulphide to dogs gives rise to this compound. Experimental details are lacking, but it should be mentioned that the action of alkali on methyldiethylsulphonium iodide evolves methyl ethyl sulphide and not diethyl sulphide.

The occurrence of methionine $CH_3S.CH_2.CH_2.CH(NH_2).CO_2H$ in nature and its relation to cysteine $HS.CH_2CH(NH_2)COOH$ and to cystine suggested that compounds containing the —SH or —S—S— links might be more responsive to the methylating action of the mould. This appeared all the more probable on recalling that glutathione, the well-known oxidation-reduction agent occurring in protein, depends for its action on the interconversion of its disulphide and reduced or thiol forms. $RSSR + 2H \rightleftharpoons 2RSH$. The result showed this expectation to be well-founded.

Recent work has established the occurrence of other S-methyl compounds in nature. Methyl β-methylthiopropionate, $CH_3S.CH_2CH_2COOCH_3$, occurs in pineapple juice (Haagen-Smit *et al.* [46A]) and the chloride of S-dimethyl-β-propiothetine

$(CH_3)_2\overset{+}{S}(\overset{-}{Cl})CH_2CH_2COOH$ has been isolated from the red alga *Polysiphonia fastigiata* by Miss M. I. Simpson and the author [49]. This sulphonium chloride (or other salt) is the precursor of the dimethyl sulphide shown by Haas [46B] to be evolved by the alga.

S. brevicaulis and Dialkyl Disulphides

Dialkyl disulphides (methyl to *n*-amyl) were added in dilute aqueous suspension to bread cultures of *S. brevicaulis*. The volatile products from the cultures were aspirated first through mercuric cyanide and then through mercuric chloride, and contained the alkylthiol RSH (absorbed in mercuric cyanide giving $(RS)_2Hg$), the unchanged disulphide R—S—S—R and the methyl alkyl sulphide $RSCH_3$. The precipitates obtained with mercuric chloride consisted of mixtures of the mercuric chloride addition product of the methyl alkyl sulphide, with varying amounts of $RSHgCl.HgCl_2$, arising from hydrolytic fission of RSSR in presence of the mercuric chloride. On treatment of these mixtures with sodium hydroxide, pure methyl alkyl sulphide was evolved and converted to the mercurichloride, the benzylmethylalkylsulphonium picrate, or the double compound with platinous chloride.

The fission of the disulphide link by *S. brevicaulis* followed by methylation appears, therefore, to be a general reaction of the simple aliphatic disulphides [47].

This biological conversion of *n*-butyl disulphide to the corresponding thiol is of interest in view of the occurrence of these two compounds and of *iso*-amylthiol in the secretion of the skunk. Traces of methylthiol are also stated to be present. Earlier workers also considered that the higher homologues of methylthiol were contained, along with basic nitrogenous compounds, in the secretions of various animals allied to the skunk. Furthermore the secretion of the zorrino, a South American marten, appears to contain a thiol with four atoms of carbon and probably the corresponding disulphide. References are given by Blackburn and Challenger [47].

Methylation of Inorganic Sulphate by *Schizophyllum commune*.

Birkinshaw, Findlay and Webb [48] have shown that the wood-destroying fungus *Schizophyllum commune*, Fr., when grown on an aqueous medium containing glucose, inorganic salts, and a trace of "Marmite", converts inorganic sulphate to methylthiol CH_3SH. This was characterised as mercury dimethylthiol $(CH_3S)_2Hg$. Traces of hydrogen sulphide are also produced. This is the only recorded instance of the mycological methylation of inorganic

sulphur. Although *S. brevicaulis* forms dimethyl selenide from inorganic selenium compounds, no methyl selenothiol is produced. F. Challenger and P. T. Charlton [49] find that dimethyl sulphide and disulphide accompany the methylthiol evolved by *S. commune*. The disulphide probably arises by aerial oxidation of the thiol.

Possible Mechanisms of Biological Methylation

Several hypotheses were considered in an attempt to elucidate the mechanism of biological methylation by moulds: (I) reaction with acetic acid, (II) reaction with formaldehyde or glyoxylic acid, possibly arising from the oxydative deamination of glycine or the breakdown of uric acid, (III) the transfer of a methyl group from some compound such as choline or betaine, already present in the tissues of the mould.

I. The Acetic Acid Hypothesis

The first of the suggested mechanisms might proceed thus in the case of arsenious acid:

$$As(OH)_3 + 3MeCO_2H = AsMe_3 + 3CO_2 + 3H_2O$$

Such a reaction would be analogous to the well-known cacodyl oxide test. Alternatively, arsonoacetic acid might result by a process of dehydrogenation:

$$CO_2HCH_2.H + H.AsO(OH)_2 = 2H + CO_2H.CH_2.AsO_3H_2.$$

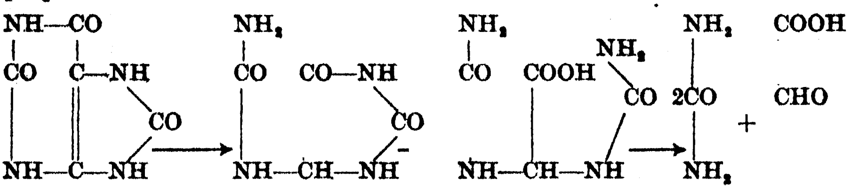
This by loss of carbon dioxide might yield methylarsonic acid $CH_3AsO(OH)_2$ which, on reduction to $CH_3As(OH)_2$, isomerization to $CH_3AsO(OH)H$, and further reduction and reaction with acetic acid, could finally yield trimethylarsine.

Challenger and Higginbottom [41] were unable to obtain any supporting evidence for this hypothesis; arsonoacetic acid in bread cultures of *S. brevicaulis* gave small quantities of trimethylarsine in some, but not all, experiments; α-arsonopropionic acid gave only traces, probably due to the formation of a little arsenious acid. Moreover, only pure trimethylarsine was evolved from cultures containing arsenious acid with salts of propionic and butyric acids, whereas on the acetic acid hypothesis some formation of triethyl- and tri-*n*-propylarsines, or even of mixed methylalkylarsines, might conceivably have been expected. It may be mentioned that thiodiglycollic acid $(CO_2H.CH_2)_2S$ gave no dimethyl sulphide. These results suggest that decarboxylation of the group $>CH.CO_2H$ does not readily occur in cultures of *S. brevicaulis*.

The acetic acid hypothesis need not be considered further.

II. The Formaldehyde Hypothesis

The view that methylation in green plants is effected by formaldehyde or by glyoxylic acid, COOH.CHO, has frequently been advanced. One may differentiate between "primary" formaldehyde produced by photosynthesis and that arising by "secondary" breakdown processes, *e.g.* by oxidative deamination of glycine. In moulds and animals any formaldehyde involved in methylation reactions is presumably of secondary origin, and even in plants some may arise by the demethylation of N > Me groups and become again available for methylation [50]. Glyoxylic acid may also arise from the oxidation of purines to uric acid which, by way of allantoin, can give rise enzymically to allantoic acid and thence to glyoxylic acid and urea, as shown by Fosse, Brunel *et al.* [51].



Uric acid Allantoin Allantoic acid

Numerous methylations can be affected by formaldehyde *in vitro*, [52]. The presence of an oxygen acceptor is necessary. This may be either formaldehyde itself, formic acid, or a suitable group present in the molecule of the compound undergoing methylation.

It has not been possible to apply a crucial test to the formaldehyde hypothesis as regards the methylations effected by moulds. In its application to the production of trimethylarsine, from arsenious acid $H.AsO(OH)_2$, this postulates the formation of hydroxymethylarsonic acid $HOCH_2.AsO(OH)_2$ as the first stage, followed by reduction to methylarsonic acid. After further reduction to $CH_3As(OH)_2$ this might be expected to react again with formaldehyde [15, 41], repetition of the process yielding cacodylic acid $(CH_3)_2AsO.OH$ and finally trimethylarsine. The formation of α-hydroxyethylphosphonic acid $CH_3CHOH.PO(OH)_2$ from acetaldehyde and phosphorous acid and of similar compounds [53] furnishes some support for this suggestion. Furthermore, hydroxymethylphosphonic acid $HOCH_2.PO(OH)_2$ is obtained by evaporating paraformaldehyde with phosphorus trichloride and adding water [54].

Unfortunately hydroxymethylarsonic acid could not be synthesised and its homologue β-hydroxyethylarsonic acid $HO.CH_2.CH_2AsO(OH)_2$ in bread cultures of the mould gives no volatile product. Challenger and Higginbottom [41], using *S.*

brevicaulis on glucose-Czapek-Dox medium containing arsenious acid, found that addition of sodium formate or of formaldehyde (free or as various derivatives), with or without formate, had no appreciable influence on the yield of trimethylarsine. If we assume that selenious and tellurous acids can react in the forms $H.SeO_2.OH$ and $H.TeO_2.OH$, the formaldehyde hypothesis can similarly be employed to explain their conversion to dimethyl selenide and dimethyl telluride in mould cultures. There is some doubt, however, as to whether selenious acid can react in this form [41], although Loevenich, Fremdling and Föhr state that β-naphthylseleninic acid $C_{10}H_7SeO_2H$ can give rise to the normal ester and also to a selenone [54A].

As applied to the fission of disulphides, and methylation of the resulting thiol, this hypothesis demands the formation of $RS.CH_2OH$. Several compounds of this type have been described [55], but are unstable and easily hydrolysed. As they could not be freed from traces of alkylthiol, their capability of reduction to $RS.CH_3$ in mould cultures could not be determined.

III. The Transfer of a Methyl Group

The transfer of a methyl group from some methylated compound such as choline or betaine was suggested by O. Riesser [56] to explain the production of creatine and of alkylated (presumably methylated) derivatives of selenium and tellurium in animals. See also F. Hofmeister [57].

F. Challenger and (Miss) C. Higginbottom [41] and F. Challenger, P. Taylor and B. Taylor [58] found that sodium sulphite, organic disulphides, sodium selenite and sodium tellurite, when heated with betaine, yielded dimethyl sulphide, methylalkyl or methylaryl sulphide, dimethyl selenide, and dimethyl telluride. The last three reactions recall the behaviour of these substances in cultures of *S. brevicaulis*, see p. 405. R. Willstätter [59] found that, on heating, betaine forms methyl dimethylaminoacetate, a reaction clearly involving the migration of a methyl group

$$(CH_3)_3\overset{+}{N}.CH_2CO.\overset{-}{O} \rightarrow (CH_3)_2N.CH_2CO.OCH_3.$$

It was suggested by F. Challenger [60] that these pyrogenic reactions might proceed as follows:

$$(1)\ Me_3\overset{+}{N}.CH_2CO\overset{-}{O} + Na_2SeO_3 = Me_2N.CH_2CO_2Na + MeSeO_3Na.$$

With selenites and tellurites a quaternary salt is possibly first formed. The dimethyl selenide presumably arises by decomposition of the sodium methaneselenonate.

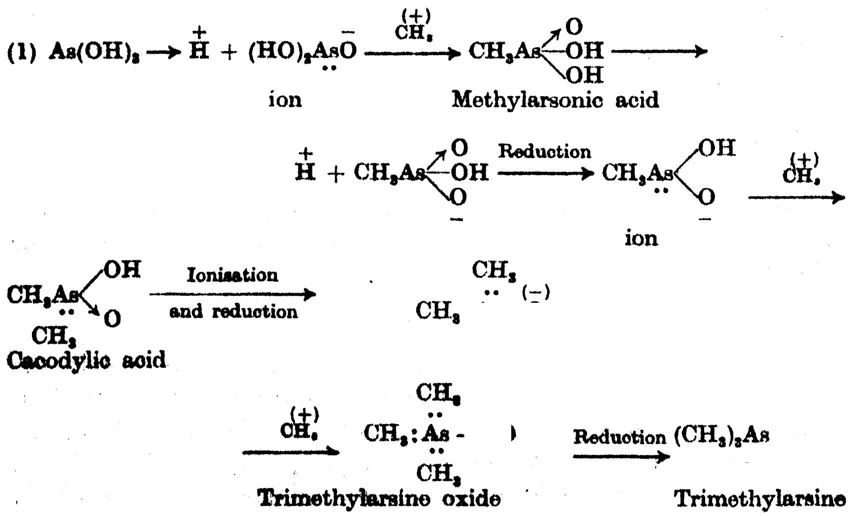
$$(2)\ Me_3\overset{+}{N}.CH_2CO\overset{-}{O} + RS.SR = Me_2N.CH_2CO_2.SR + RSMe.$$

Under similar conditions primary aromatic amines yielded *N*-monomethyl derivatives.

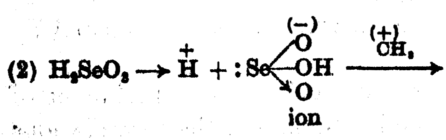
In the absence of any evidence as to the kinetics of these pyrogenic betaine decompositions, it is impossible to decide upon the mechanism by which the methyl group is transferred. Experimental evidence is equally lacking as regards the kinetics of the production of methyl derivatives by living cells. Considering first a unimolecular mechanism of the type discussed by Ingold and his colleagues [61] it is noticed that almost all the compounds which undergo methylation by moulds or animals can give negative ions, which contain unshared electrons, so that co-ordination of a positive methyl group would give a neutral molecule [62]. This could then undergo reduction and ionisation followed by further co-ordination of a $\overset{+}{C}H_3$ radical.

Methylation of Arsenic, Selenium and Tellurium Compounds

The mechanism suggested by the Leeds School [62] may be illustrated in the case of arsenious and selenious acids :



The suggested intermediate compounds have not been detected in mould cultures, but they all yield trimethylarsine when present in bread cultures of *S. brevicaulis*.



$$CH_3Se\begin{matrix}\nearrow O\\ -OH\\ \searrow O\end{matrix} \xrightarrow[\text{and reduction}]{\text{Ionisation}} CH_3Se\begin{matrix}\nearrow \bar{O}\\ :\\ \searrow O\end{matrix} \xrightarrow{\overset{(+)}{CH_3}}$$

Methaneselenonic acid — Ion of Methaneseleninic acid

$$(CH_3)_2Se\begin{matrix}\nearrow O\\ \searrow O\end{matrix} \xrightarrow{\text{Reduction}} (CH_3)_2\ddot{Se}:$$

Dimethyl selenone — Dimethyl selenide.

The postulated intermediate selenium compounds have not been detected in the media, but (Miss) M. L. Bird and F. Challenger [63] showed that *S. brevicaulis* and certain *Penicillia* convert methane-, ethane-, and propane-l-seleninic acids, $RSeO_2H$ to dimethyl-methylethyl-, and methyl-*n*-propyl selenides RSeMe, as required by the suggested mechanism, thus:

$$RSe\bar{O}_2 + \overset{+}{C}H_3 \longrightarrow R.SeO_2.CH_3 \xrightarrow{\text{Reduction}} R.Se.CH_3$$

Potassium methane-, ethane-, and propane-l-selenonates [64] $RSeO_2.OK$, in cultures of the same moulds, gave only dimethyl selenide, due to breakdown of the selenonate giving R.OH and $KHSeO_3$. This observation does not necessarily invalidate the suggested mechanism, since the methaneselenonic acid might be sufficiently stable, within the cell, to reach the next stage without hydrolysis.

Methylation of Sulphur Compounds

The methyl alkyl sulphides obtained from dialkyl disulphides in cultures of *S. brevicaulis* may arise by ionisation of alkylthiol first produced, followed by co-ordination of CH_3^+, or this may occur prior to fission (58).

Methylation of Nitrogen Compounds

Co-ordination of a positive methyl ion would also explain the well-known conversion of neutral pyridine and quinoline to methylpyridinium and methylquinolinium hydroxides in the body of the dog. The formation of trigonelline or N′-methylnicotinamide on administration of nicotinic acid to various animals may be explained in the same way (see p. 402).

Alternative Mechanisms of Biological Methylation

One alternative to methylation by elimination of a positive methyl ion is a bimolecular reaction, of the type also discussed by Ingold and his colleagues [61].

Since, however, this also ultimately involves the attachment of methyl to the unshared electrons of the metalloid, the formulations

given above may be retained for convenience in representing the suggested intermediate stages in the methylation process. It is possible, however, that methyl may be transferred as a neutral radical. Attempts to obtain evidence of this by addition of sulphur, in powder or as a colloidal solution, or of finely divided mercury to cultures of *S. brevicaulis* gave negative results, no methylated compounds being detected.

As pointed out by Mr. J. H. Baxendale (private communication) the capture of a neutral methyl group by a negative ion, *e.g.* arsenite, would give nine electrons on the arsenic atom, an unstable system which would act as a strong reducing agent, readily forming neutral methylarsonic acid $CH_3AsO(OH)_2$. This might possibly be concerned in the reducing actions which cultures of *S. brevicaulis* obviously exert upon the higher valencies of arsenic, selenium and tellurium, inorganic arsenates, selenates and tellurates yielding organic arsines, selenides and tellurides.

Transmethylation. Du Vigneaud's Experiments using Isotopic Indicators

Transmethylation from Methionine and Choline

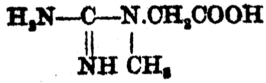
The suggestion that certain biological methylations in animals might be conditioned by methyl groups detached from choline or betaine [56] received support from the work of du Vigneaud and his colleagues. They have shown [65] that homocystine (I) can replace methionine (III) in the diet of the white rat only in presence of choline or betaine, which, however, produces the effect more slowly than choline. It was suggested that a methyl group is transferred from the nitrogen of choline or betaine to the sulphur of homocysteine (II) ("transmethylation") to give methionine, and that the reaction might be reversible, methionine acting as a donor of methyl groups to a choline precursor.

$(CO_2H.CH(NH)_2.CH_2.CH_2S)_2$
(I)

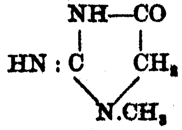
$CO_2H.CH(NH_2).CH_2CH_2SH$
(II)

$CO_2H.CH(NH_2)CH_2CH_2S.CH_3$
(III)

$CO_2H.CH(NH_2)CH_2.CH_2.SCD_3$
(IV)



(V)



(VI)

V. du Vigneaud's "transmethylation" hypothesis was tested by the use of specimens of deuteriomethionine (IV) containing (*a*) 83·6

and (*b*) 87·5 atom per cent. of deuterium in the methyl group. These were fed to rats kept on a methionine-choline-free diet [66]. Earlier work had shown that the deuterium content of the urinary creatinine (VI) closely follows that of the creatine (V) and choline of the tissues. The experiment with specimen (*a*) was, therefore, continued for 94 days until the methyl group of the creatinine contained 72·4 atom per cent. The animal was then killed and the choline isolated from the tissues as the chloroplatinate. The atom percentage of deuterium in the methyl groups of this choline was found to be 74·2, the corresponding figure for the tissue creatine being 73. These figures represent in all three cases approximately 83 per cent. of the theoretically possible amount of deuterium, assuming that all the methyl groups had come from the deuteriomethionine. This figure is the "deuterium ratio," *i.e.* atom per cent. deuterium in methyl group of isolated compound/atom per cent. deuterium in methyl group of deuteriomethionine administered × 100. Oxidation of the choline to trimethylamine showed that all the deuterium was contained in the methyl groups.

It is concluded that these reactions are true transmethylations (the methyl group being transferred as a whole), and that they do not involve the elimination of dideuterioformaldehyde CD_2O. On the formaldehyde theory of methylation, dideuterioformaldehyde, if produced, would react with the amino-group of the choline precursor, presumably ethanolamine $HOCH_2CH_2NH_2$ [67], to give $—NHCD_2OH$, which on reduction in the organism would give $—NHCD_2H$ and not $—NHCD_3$. The deuterium content of each methyl group of the choline could not then rise above two-thirds of that in the methyl group of the methionine administered, *i.e.* the "deuterium ratio" would have a maximum of 66·6 per cent.

V. du Vigneaud *et al.* [68] then administered trideuteriocholine $(CD_3)_3\overset{+}{N}(\overset{-}{O}H)CH_2.CH_2OH$ to rats, on a methionine-choline-free diet containing homocystine, for 23 and 56 days respectively. On isolation of the creatine (V) from the tissues the deuterium content was 24 per cent. and 29 per cent. of the theoretical maximum and the deuteriomethyl group was detected in tissue methionine. The methyl groups of choline can, therefore, take part in transmethylation. This also occurs, to a lesser extent, when no homocystine is given or when ordinary methionine is given instead of homocystine.

The authors consider that homocysteine is formed from methionine by the animal, and that methionine is re-formed by means of the methyl group, supplied by choline. Continuous synthesis of methionine, therefore, occurs although more than enough is supplied in the diet. When deuteriomethionine and an

adequate supply of ordinary choline were fed together, formation of choline from methionine was found to proceed nevertheless.

The occurrence of transmethylation has also been established in the rabbit [69] by the use of deuteriomethionine (79 atom per cent. D in the methyl group), and analysis of the creatinine of the urine and the choline of the tissues. Later Simmonds and du Vigneaud [70], using the isotope technique, showed that the methyl group of dietary methionine can be used by man in the synthesis of choline and creatinine.

V. du Vigneaud *et. al.* [71] fed dimethylaminoethanol to young rats on a methyl-free basal diet containing homocystine. Growth was not so good as when choline was fed, *i.e.* methionine was less readily formed. However, deuteriodimethylaminoethanol $(CH_2D)_2N.CH_2CH_2OH$ under similar conditions was readily converted to a deuteriocholine and thence to creatine by transmethylation. Presumably dimethylaminoethanol does not take part directly in transmethylation, but can accept methyl groups supplied by methionine or some other methyl donor in the body, thus giving choline and accounting for the limited growth observed. If so, it follows that choline, when engaging in transmethylation, releases only one methyl group giving dimethylaminoethanol. Experiments with deuteriomonomethylaminoethanol $CD_3NH.CH_2CH_2OH$ led to similar conclusions. The incapacity of the partially methylated aminoethanols to transfer their methyl groups may be due to the absence of the quaternary nitrogen atom which is present in choline and betaine.

Transmethylation from Betaine

Final proof that betaine takes part in transmethylation has now been obtained. The early experiments of du Vigneaud [65] pointed clearly in this direction. Stetten [67] showed that on administration of betaine containing N^{15} to rats the concentration of this isotope in the glycine of the tissue-protein was almost as high as when isotopic glycine was fed, thus proving demethylation of the betaine. V. du Vigneaud *et. al.* [72] fed betaine labelled with deuteriomethyl groups and N^{15} to growing rats. Isotopic analyses of the choline and creatine isolated from the rat tissues showed betaine to be a very effective methyl donor. Methyl groups from dietary betaine appear in tissue choline almost as rapidly as they appear from dietary deuteriocholine. The disparity in the amounts of N^{15} and of deuterium found in the tissues proves that the betaine molecule is not converted as a whole to choline.

The methyl group of dietary methionine appears more rapidly

in creatine [73] than do those of dietary betaine. Very possibly the transfer of methyl groups from choline and betaine to form creatine involves transmethylation forming first methionine and then, either directly or indirectly, creatine [74].

CONCLUSION

The work summarised in this article has exemplified the principal types of reaction in which biological methylation takes part. The work of du Vigneaud and his colleagues has clearly established that the relations between methionine, choline, betaine and creatine in the animal body involve transmethylation, and that in the particular reactions studied, and under given experimental conditions, this does not proceed by elimination of formaldehyde. Recent work in England and in America suggests that transmethylation may also be of importance in the biochemistry of cancer and especially in a study of the action of carcinogenic compounds [75, 76, 77].

The mechanism by which methylation is effected by moulds is still uncertain, nor is any decision likely until the results of experiments using labelled substrates, at present in progress, are available.

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SOME PROBLEMS OF ROCKET PROPULSION*

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THERE are many points of scientific and psychological interest arising from the use of rockets for military purposes. It is possible to write at considerable length upon each of them, but a detailed discussion of any one aspect might tend to leave an unbalanced point of view. I, therefore, propose to discuss not one, but several of the problems involved and to touch only lightly upon each of them.

I have therefore attempted to formulate the questions which, I imagine, are in the minds of those who either care to think about rockets, or who are compelled by circumstances to do so, and then to set myself the task of indicating the general nature of the answers. The queries which I postulate are—What is a rocket ?—How does it work ?—Why does the use of rockets in war appear to arouse feelings of terror ?—What are the advantages of utilising the rocket principle of propulsion ?—What is likely to be the nature of further developments in rockets ?

In my answers I shall try to bear in mind the special requirements of conditions of war and peace.

In the first instance, may I repeat what is presumably common knowledge, namely that the rocket is not a new invention. Signal rockets have been known for thousands of years, their first use dating, it is understood, from the time of the invention of gunpowder by the Chinese. They certainly antedate Confucius who lived about B.C. 500. In the early days rockets were used either to scare away evil spirits or to importune the Gods. This same method of drawing attention to spiritual and material needs is practised in Nepal even at the present time. A sketch of the principal features of a primitive rocket is shown in Fig. 1.

Although the practical application of the rocket principle is very old, the understanding of its method of operation did not come until Newton expounded it. The basic principle is " To every action there is an equal and an opposite reaction ; or, the actions of two portions of matter on each other are always equal and are exactly opposed."

* The writer is indebted to the Chief Scientist, Ministry of Supply, for permission to publish this essay.

In their non-spiritual aspects, rockets seem to have been used almost entirely as weapons of war. Their use in this respect probably antedates that of guns. A German monk, Berthold Schwarz, is usually given whatever credit there is for the invention of guns; the date is usually stated to be a little after A.D. 1300. The use of rockets, however, is mentioned in a Chinese chronicle describing the battle of Kai-Fung-Fou, which took place in A.D. 1232. Rockets were certainly recognized and used for military purposes by the end of the fourteenth century; they are described in Von Eichstädt's *Bellifortis* of 1405 and in de Fontana's *Bellicorum Instrumentorum Liber* of 1420. The latter goes so far as to describe flying rockets disguised as pigeons —a development of which the details have not so far been recovered by 20th-century investigators. However, by the early seventeenth century, rockets as a military weapon had fallen into disfavour, but their use in pyrotechnics continued. The making of gunpowder rockets, stabilised by controlling sticks, was described by Hanzelet Lorrain in 1630, and they are made in much the same way at the present time.

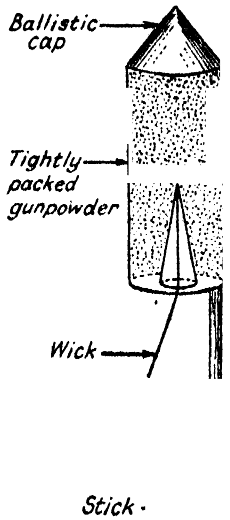

FIG. 1.

The modern phase in the history of military rockets began around 1800, and their use is associated with the name of Sir William Congreve. His interests were aroused by reports of effective rocket fire by Indian troops against the British, and he was the inspiring force behind the development of military rockets for British forces. His largest were about 200 to 300 lb. in weight and attained a range of over 3000 yards. These rockets were used at Leipzig and Danzig in 1813. They were first tried out in 1809 at the siege of Flushing. The expedition reponsible for the trial was a costly failure, and is remembered chiefly for the terrible sickness from which the force suffered. But the siege and capture at Flushing was a triumph for the Siege Artillery, for the batteries opened at midday on August 13, and the place surrendered on the morning of the 15th!

It is interesting to note that Sir William Congreve was a civilian. He was never an officer of a regiment; he succeeded his father as Comptroller of the Royal Laboratory and was responsible for many

artillery inventions. The professional gunners of that time were not very enthusiastic, in fact their reports were very damning, and the rocket as a weapon of war fell into disrepute. They were, however, used in the American War, particularly against Fort McHenry; the words of the American Anthem, "the rockets' red glare, the bombs bursting in air", refer to Congreve rockets. They were re-introduced, however, about the 1870's, by a Mr. Hale and became service stores at that time. They again became obsolete about 1890.

Many governments have attempted to develop the rocket and so, in the competition for new and more effective armament, attempts to develop rockets never really ceased. In America research proceeded, I understand, quite as actively as in European countries. In England serious attempts to develop rockets seem to have started only shortly before the beginning of the 1939 World War. In the interval between the American Civil War and the 1914 World War two developments took place which revolutionised the technique of armament. The first was the development and application of modern metallurgical techniques and the second was the introduction of colloidal propellants by Vieille in 1886. The British name for this propellant is "cordite"; the Americans call it "smokeless powder". The American term "powder" derives from the first type of propellant, "gunpowder". All propellants in American technical language are called powders. Cordite was called "smokeless" not because it produced no smoke, but because it produced less smoke—so that the American name is logical after all. In fact, in the very early days discharges of gun-powder produced terrific clouds of carbon, and for this reason were called "black-boxers", no doubt in recognition of eminent coloured pugilists.

During the 1914 World War, attempts were made on a small scale to use rockets attached to the inter-plane struts of aeroplanes. They were fired electrically by the pilot. About four rockets were mounted on each side. Their best range was under 400 feet; beyond this the curved trajectory of the rocket made accurate aiming impossible. They were known as "Le Prieur" rockets after their inventor, Lieut. Y. P. G. Le Prieur of the French Navy. References can be found in the official book *War in the Air*, and also in *Jane's Book of the World Aircraft of 1919*. The use of rockets on aircraft is also mentioned in contemporary war novels such as Gilbert Frankau's *Peter Jackson, Cigar Merchant*.

I should now like to turn to my first question, "What is a rocket?" In principle, a rocket must consist of a container or chamber in which gases are generated at high pressure, and in

which there is some sort of a vent or nozzle through which the gases may escape in the form of a jet. This part of the assembly provides the propelling force, and for this reason is usually called the motor of the rocket. A rocket may also have a "head," containing apparatus of one kind or another, ranging from apparatus to determine weather conditions, radio devices, wire devices, parachutes,

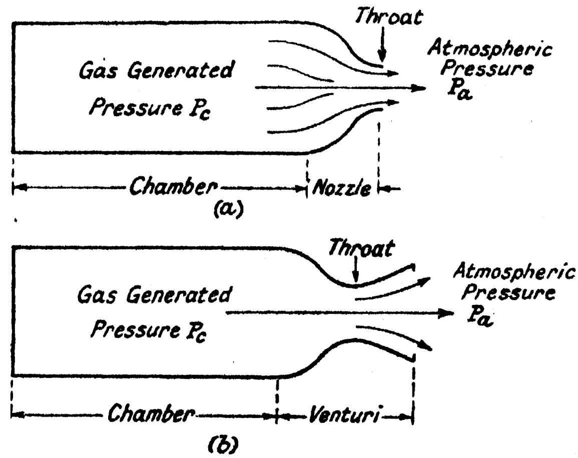

FIG. 2.

flares, to high explosives, etc. Fig. 2(*a*) shows a diagram of the essentials of a rocket motor. The converging section is called a "nozzle." Sometimes an expanding cone is attached to the nozzle, as in Fig. 2(*b*) and the convergent-divergent system is called a "venturi." In order to appreciate the importance of the nozzle, let us consider one or two simplified cases. Let us assume that, in the first instance, the chamber is just filled with still air at atmospheric pressure and that we have at our disposal a device for pumping air into the chamber. At first the pressure is the same inside and outside. We next pump in air at a slow steady rate. It will tend to accumulate inside the chamber and so build up a pressure there. On the outside of the nozzle we have air at atmospheric pressure and on the inside we have air at a higher pressure; there will, therefore, be a flow from the chamber to the outside, and after a little time a steady state will have been set up whereby, corresponding to the rate of introduction of air, there will be a steady pressure in the chamber and a steady rate of flow to the outside air. Suppose now that we experiment and increase the rate of input of air to a second constant value. Sometime later a second steady flow will have been set up—and so we can go on varying the input

of air and getting a series of steady states. It can be shown by very simple theoretical considerations that the various characteristics of these steady states are given qualitatively by the curves of Fig. 3. The important point to notice is that, if the pressure in the chamber exceeds a certain value P*, the velocity of the gases at the throat is unaffected. It is as if with that critical pressure

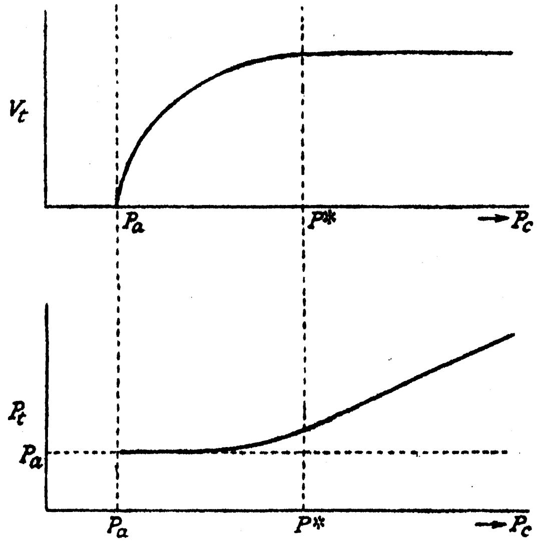

FIG. 3.

V_t = velocity at throat, P = pressure at throat, P_a = atmospheric pressure, P_c = chamber pressure, P* = critical pressure.

the throat of the rocket takes charge of the whole proceedings and insists that all the gases which pass through it shall do so at a velocity fixed by itself. "It nozzles the flow." For any nozzle, therefore. there appears to be a maximum velocity of efflux. The rate of discharge of matter however, depends upon the area of the nozzle throat, upon the velocity of efflux and upon the density of the emergent gases, so that by increasing the density of the gases, that is by building up the pressure within the chamber, one can attain very considerable rates of mass discharge even though the velocity of efflux remains constant.

Here arises the first important problem of rocket propulsion. How must the nozzle be designed? Upon what principles should the design be put forward? This depends upon a very thorough understanding of the nature of the flow at the entry to the nozzle. Up to the present we have no true guide, but engineers have [illegible] a very simple form of entry which produces overall results

which are in accordance with our general expectations. There is reason to believe, however, that there may be a considerable loss of energy due to turbulent interchange in the nozzle entry.

The second problem arises from the desirability of having a complete understanding of the flow and pressure inside the chamber. Even that is lacking, though considerable progress in this direction has been made. The importance of a knowledge of the flow lies in the fact that it is desirable to make the walls of the chamber as light as possible and yet able to withstand as high a pressure as practicable. This introduces questions of hydrodynamics, metallurgical techniques and heat flow. The question of heat flow is of dominant importance, because the gases which are generated are usually very hot, and if the combustion inside the rocket chamber lasts for any length of time the heat softens the metal and makes it less able to withstand the internal pressures than in the cold state. Arising from this comes a new series of problems. For example, if the gases have a certain temperature and chemical composition, what is the type of metal which should be used in order to avoid chemical action between the gases and the container ? Is it possible to devise some form of refractory lining to the chamber which is impervious to the flow of heat, or which will so delay the flow of heat that, by the time the metal of the chamber is very hot, the generation of gases inside the chamber will have ceased and the pressure will have dropped below the value at which safety is endangered ?

Then there is the question of the means to be adopted to produce the generation of gases. Should the gas come from a tight wad of propellant pushed into the back of the chamber, burning from one face only ? Or should we use specially shaped charges inside the chamber, burning over their whole surfaces ? Or should we have fluids inside, so arranged that they are pumped out of their containers to react chemically when they mix in a small internal chamber ? These are the kinds of problems which have held up the development of rockets and I think it is fair to say that in very considerable measure they have been solved in principle.

The efficiency of the system as a whole, however, is not very great ; the amount of energy which it has been possible to use for propulsive purposes is only a small fraction of the total energy known to be contained in the propellant. The search for new types of propellant and for improved variants of existing types still continues. I think that it is not incorrect to say that up to about 1942, this country was in the lead as far as rocket development was concerned, and that this was principally due to the excellent

work of British chemists in producing a colloidal propellant much more reliable in action and much more safe to handle than similar propellants produced in other countries, and also due to the fact that they had perfected the technique of manufacture of cordite in large sizes, something which until a few years before the 1939 war had been considered virtually an impossibility. All the results of British investigations into rockets were handed over to American and Russian authorities during the last war, and it is more than likely that at the time of writing Great Britain no longer leads in the technical development of rockets.

Let us, however, revert to our consideration of the rocket nozzle. The gases which emerge from it do so with high velocity and with considerable thermal energy. If we could convert some of this thermal energy into dynamic energy we should increase the velocity of ejection. The object of increasing the velocity of ejection is to increase the action on the rocket chamber. That this is so can be seen very briefly from Figs. 4 and 5. The increase in velocity is achieved by fitting an expansion cone to the nozzle and the gas which emerges from the throat converts some of its heat energy into dynamic energy, and within a matter of inches it is possible to increase the velocity from something of the order of 3000 feet per second to something of the order of 6000 feet per second by these means. In fact, by adding a small expanding cone to the system one can increase the total thrust by something of the order of 20 to 25 per cent.

Here arises an entirely new set of problems. What is the best angle of divergence for the expanding cone? If the cone is too narrow the rocket will lose thrust and we shall increase the friction between the propellant gases and the metal walls of the cone. If the cone angle is too wide, the jet may not fill the whole cone and may, possibly, sway from side to side, so that in its flight through the air the rocket will be subject to the influence of some forces whose line of action wobbles considerably. This will produce erratic flight, a phenomenon seen by large numbers of people at about November 5 of each year! Here then is another of the principal problems of pure science in rocket development.

At this stage I would like to devote a little time to a discussion of the actual flight of rockets and to indicate briefly the nature of the problems which arise.

The first problem in ballistics as applied to rockets is, of course, to determine by calculation how far any specific rocket will go. The calculations required for this are somewhat different from those for guns. In a gun cordite is ignited and completely burnt in a

confined space. Gases are generated at very high pressure and this pressure acts uniformly in all directions. It acts backwards on the closed breech of the gun and it acts forward on the shell. The gun is pushed backward and the shell is pushed forward. The shell is able to move along the barrel of the gun but, by the time it reaches the muzzle, all the cordite behind it has been consumed, so that

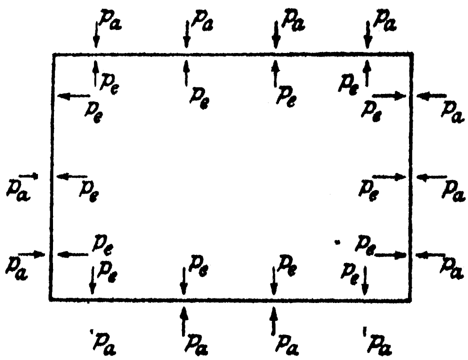

FIG. 4.

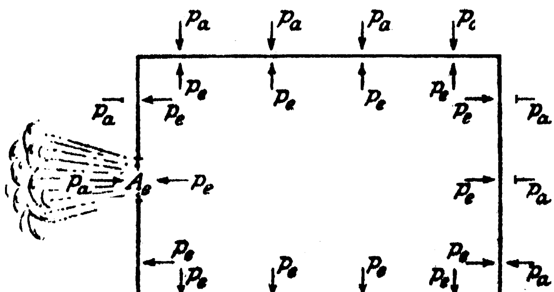

FIG. 5.

Q = rate of discharge of mass, W = velocity of efflux of gases, A_e = area of exit, P_e = at exit, P_a = atmospheric pressure

Static thrust: $A_e(P_e - P_a)$

Total thrust: $QW + A_e(P_e - P_a)$

when it is clear of the muzzle there is no further propelling force on the shell. In fact, at the muzzle the shell has its maximum forward velocity along its trajectory. From a knowledge of this maximum forward velocity, which can be determined either by empirical calculations or by direct photographic measurement, and from a knowledge of the air resistance on shells of various types, it is possible to calculate how far the shells will go. The problem for

guns, therefore, is comparatively easy. For rockets the calculation is rather more complicated. The cordite is ignited in a chamber which is open at one end and closed at the other. The force exerted by the motor provides the forward driving force. At the open end there is a loss of matter produced by the expulsion of gases at high pressure. The rocket starts to move as soon as the forward driving force is large enough to overcome friction and the retarding component of gravity; it goes forward under a comparatively small accelerating force. In the gun, for example, the accelerating force on the shell is many thousands of times that of gravity. In the ordinary rocket it is something of the order of 20 or 30 or 40 times that of gravity. For the German V2 weapon, the resultant vertical acceleration in the early stages of flight is only approximately half that of gravity. However, the time during which the propulsive force acts is quite different in rockets from that in guns. In guns there is a large force acting for a very short time, several thousandths of a second; in rockets the time can be varied very considerably by altering the shape of the charge, the dimensions of the chamber and the size of the nozzle. In existing rockets the time varies from a third of a second to two seconds. In the V1 weapon, which also employed the method of jet propulsion, the time was as high as twenty minutes. In the V2 rocket the time was of the order of five or six minutes. It can readily be appreciated, therefore, that the kinds of technical problems which arise differ very considerably. In fact, with an increase in the time of burning there arises a host of new metallurgical problems, and it becomes necessary to devise systems which will stand up to the intense heat generated by the propellant gases for very considerable lengths of time. Here, too, is one of the major problems of rocket propulsion.

Returning to the question of flight, however, we see that a rocket is subject to an accelerating force for a much longer time than a shell. Hence, even though it may start off with a small acceleration, it may ultimately reach a velocity comparable with that of a shell. If it becomes necessary to compare the motion of shell and rocket, attention must be concentrated upon that point in space where the cordite of the rocket is completely burnt up. A little to the rear of that point, the resultant forward acceleration becomes zero and the rocket then attains its maximum forward velocity along its trajectory. That point, which may be 500, 1000, or 1500 feet away from the point of projection, corresponds to the muzzle of the ordinary gun. From that point onwards the motion of a rocket obeys the same kind of rules as the motion of a shell.

In reaching that point, however, there are fundamental

differences. During the time in which the shell is being accelerated it is constrained on all sides by the barrel of the gun—which is a precision instrument. The rocket, however, may be constrained for only the first few feet of its flight, depending, of course, upon the length of the rails on which it rests. In fact, some rockets may be constrained for only a few inches, the length of the projector being determined from considerations of the space available, say in aeroplanes or on ships. Even when it leaves the projector the rocket is still moving comparatively slowly and is subject to the very variable winds which occur in the region of the projector. Rockets, therefore, are very considerably disturbed in the region of the lower atmosphere. The determination of atmospheric variations within 100 feet of the surface of the earth presents the next really important scientific problem if we are to have a thorough understanding of the motion of this form of projectile. The matter is further complicated by the fact that the gases which are shot out of the rear of the rocket may be travelling at speeds of the order of 5000 to 6000 feet per second, whereas the rocket may be moving forward from the end of the projector with a speed something less than 200 feet per second. It can, therefore, be visualised that the propellant gases may easily be reflected from objects in the neighbourhood of the rocket and then be shot forward to overtake the rocket, which may, therefore, be travelling in an atmosphere disturbed not only by the wind but by its own propellant gases. On general grounds, therefore, we should expect the rocket to be a less accurate weapon than the shell—and this has turned out to be the case. It should be noted that shells, by contrast, pass through the highly turbulent region with their greatest velocity, and are, comparatively, extremely accurate.

From the point of view of ballistics, pressure determinations can be made along the barrel of a gun and a time-record of the forces on the shell can be evaluated. In the case of the rocket the same effect can be achieved, but by different types of apparatus, so that in both cases the maximum velocity can be calculated with appropriate degrees of accuracy. The remainder of the path can be calculated according to the same system of rules, but here again the information at our disposal on the resistance experienced by bodies of various shapes at speeds greater than that of sound is very meagre, and it is rather surprising that with this scanty information the experts are able to make such accurate predictions of ranging. Here too lies an important problem of rocket motion involving the determination of aerodynamic resistance by laboratory experiments, or by mathematical calculation. This problem is assuming greater

importance as the attention of governments and aeroplane firms is being directed to the question of supersonic motion. There are signs, at the present moment, of serious attempts all over the world to solve these problems.

There is, however, another aspect of the ballistics problem. Prediction of range in itself is not enough; one must have accuracy in fall of shot. For example, if a shell leaves a gun in a prescribed direction, with a known velocity, it is not enough to be able to predict how far away from the projector it will fall—one must attempt to predict the precise point where it is going to fall. If an ordinary shell were shot forward with some known velocity and no special precautions were taken, it would turn over and over in the air—just as does a walking-stick when it is thrown into the air. The centre of gravity of the shell would move along some curve. That curve would be influenced by the actual aerodynamic resistance experienced by the shell, and because the shell would roll round and round in the air the resistance would be increased and the ranging diminished. However, the shell would experience no difficulty in getting away from the projector! In the case of rockets, however, the position is a little more spectacular. Consider a rocket which leaves the projector and rolls round on its path while still under the influence of its propulsive force. As it diverges from its original path the accelerating forces will propel it in this new direction with an increased velocity. If it again deviates from its path it will go still faster in its final direction. In fact, if great care is not taken, a rocket can depart very considerably from its expected path. In order to avoid the occurrence of such phenomena one attempts to "stabilise" the weapons. As is well known, a shell is stabilised by spinning, that is, as it travels along the barrel it is constrained to spin around its axis, the rate of spin being calculated to give the required degree of stability. The rocket can also be stabilised by spinning, or it can be stabilised by fins, as is the dart, or it can be stabilised by a trailing stick as in the primitive rockets. It can even be stabilised by a trailing string. The object of the fins, the stick or the string is this: if the rocket departs slightly from its calculated path, the fins, for example, experience increased aerodynamic forces in a direction such as to counteract the effect of the deviation. The precise calculation of the size of fins required for this purpose is a matter of considerable complexity, and the matter has had to be approached almost entirely from the empirical point of view. If the fins are too small they do not damp out disturbances in flight sufficiently rapidly. If they are too large they add considerably to weight and to resistance, and so reduce

the range. In addition, large fins increase the susceptibility of the rocket to variations of wind in the lower atmosphere. One has therefore to strike a compromise between the requirements of ranging, of damping out disturbances and of the effects of the lower atmosphere.

In considering the question of accuracy it is essential that the resultant forward force should, in all cases, pass through the centre of gravity of the rocket. If it did not do so there would be a turning moment about the centre of gravity and the rocket would turn round very considerably. As the position of the centre of gravity in a rocket varies very considerably during its flight, due to the consumption of its propellant, the problem of ensuring that the thrust always acts through the centre of gravity is a rather complicated one, and a thorough understanding of the magnitudes of the factors tending towards an increase or reduction of accuracy is absolutely essential.

So far, I have attempted to outline the problems which arise in a full investigation of rocket propulsion. Then the question arises, or should have arisen at an earlier stage, " What are the advantages of utilising the rocket principle of propulsion ? " For conditions of peace there are many potential advantages arising from the fact that the propulsion unit, the motor, is much simpler than the present conventional engine, the weight and cost for a given horse-power being much reduced. This means that for a given overall weight of unit it should be possible to generate a much greater horse-power than with the conventional type of engine. It seems to me that for some time to come the jet method will have its principal application in aeroplanes, ships and, possibly later, in trains. With improvements in types of propellant it is also possible that motor-car traffic might in due course be transformed.

For conditions of warfare, the principal advantage lies, in the first instance, in the lightness and in the cheapness of the projector. In making this remark I have in mind not only " money value", which may be fictitious, but also the value as measured in man-hours of work. In place of a gun, which has to be a precision instrument carefully machined and adjusted and costing many thousands of pounds, one can use a most primitive-looking apparatus costing some thirty or so pounds, which is equally effective. The reduced weight of rocket projector as compared with the gun tends to greater mobility of batteries. It tends to increase the size of salvoes and so enables areas to be neutralized with greater speed. It also makes possible the fitting of the equivalent of very heavy armament to aeroplanes. In this connection the absence of recoil,

or rather the absence of a closed breech to take the backward force arising in projection, is the essential characteristic which makes it possible to simplify the construction of the projector.

It should be realised also that a normal gun has a limited accuracy life; every shot tends to disturb the trueness of the bore and after a certain number of shots a gun needs a major operation to make it useful. For rocket projectors there is a much greater accuracy life and the cost of replacement is trivial.

The use of the rocket system of propulsion enables one to apply a sustained motive force to a projectile instead of the impulsive force usual in the gun. This makes possible the introduction of long-range projectiles and also of guided projectiles, that is, guided by electrical or other devices. The absence of the very large accelerating forces which occur in the barrel of a gun makes it possible to fit to the rocket head many complicated electrical devices, which would be broken if put into the shell of a gun.

The sustained motive force also makes possible the use of the rocket principle for under-water motion.

The simplicity of the rocket projector means that in times of war training is no longer a very arduous task, and is completed much more quickly than with the conventional type of gun.

It has been said that the greatest limitations upon rockets, as we know them, are their comparative inaccuracy, and the considerable illumination which they produce when fired. I am not in agreement with either of these strictures. We must look upon these two properties as characteristics of the weapon for some time to come, and our problem is to determine whether or not we can take advantage of them. In my mind at any rate, there is no doubt whatsoever that the comparatively large dispersion of the rocket is in many cases extremely advantageous. I feel that the gun, possibly surprisingly, is much too accurate. The positions of most targets are hardly ever known accurately; they are usually known to lie within a certain area on the ground or within a certain volume of space. For targets such as these, the only weapon to use is one which has a wide dispersion—upon the principle that a shot-gun is used to shoot birds rather than a high-powered accurate rifle. If one has to view the problem dispassionately, one must rid one's mind of the fetish of accuracy. One has to concentrate upon the conditions of the problem as they are rather than upon the idealised ones which, up till recently, have been the concern of gunners.

Then there is the question of illumination and flash, and the fact that very often the rocket can be seen rising through the skies gathering speed. Attempts have been made to produce types of

propellant which will not give rise to considerable illumination. I am not at all sure that this is a wise step. Psychologically the fact that one can actually see the approach of the projectiles which are known to be going to burst all round one is very unnerving, and the advantage in war lies with the one who can most unnerve his opponent. In this respect also the fact that rockets go more slowly than shells, and can be seen at the target end as ugly projectiles which are approaching, apparently inescapably, gives them their terror-making characteristics. The shell or the bullet which makes its presence felt only after it has arrived is, by comparison, much less terrifying. This has been confirmed by many prisoners of war.

If the future holds another major war in store for us, then I feel that rockets will be used much more extensively than in the past. They will not supersede shells, but will take over many of their rôles. The two forms of armament will supplement each other and will on the whole form an effective combination. The essential point involved in the use of rockets will be that, if their accuracy is not improved, they will have to be used in large numbers, and the cost of warfare will be even greater than in the past. Similarly, for long-range rockets, if their use in warfare is to be justified on some form of economic balance, countries will have to convince themselves that the net result justifies the expenditure of money and man-hours. On the whole I feel inclined to suggest that for many years to come rockets are not likely to be accurate, so that their use will hang upon the destructive power of their war heads. If the damage is localised, rockets are not likely to have an effective part to play in the ultimate decision. They will be, in the main, nuisance weapons of which the object will be to divert air forces from more effective use.

Another point to consider is that, as the range is increased, the size of the weapon goes up very considerably. The increase is not directly proportional to the increase in range. For any specific design it is probably somewhere nearer the cube of the range. As an example, consider the German weapon V2—a weapon of some 12 tons was required for a maximum range of about 250 miles. If a weapon has to be designed to go 500 miles, the overall weight is likely to be something of the order of 100 tons, and so on. There may even be a maximum range beyond which no weapon of this design can go. Here again the economics of warfare come forward as the outstanding factor, and it is my hope that if the nations of the world cannot agree to live in amity, guided by principles of religion or common-sense, then at least they will be forced to the same end by considerations of the cost of warfare.

As far as peace is concerned, the use of the rocket system of

propulsion makes possible the realization of the world of fancy created by writers like H. G. Wells. It is not beyond the bounds of possibility that satellite ships will cruise over the surface of the world beyond the limits of the earth's atmosphere. It may possibly be that when we have solved the problems of this world those of the human race who wish to satisfy their urge to discover new things will find within the rocket system of propulsion the tool for their job. But that is looking somewhat ahead—there still are many problems to be solved on this earth, not the least of which is the arranging of conditions of life in such a way that nations no longer use war as a means of settling differences, so that the rocket system of propulsion will be used to satisfy only the peaceful needs of society.

THE PROBLEM OF POLLUTION OF WATER

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Britain's Water Supply

In Great Britain the majority of the population is provided with a piped supply of water, which is generally sufficient in quantity and satisfactory in quality. The volume distributed daily by water undertakings is of the order of 1,500 million gallons; of this some two-thirds to three-quarters is drawn from rivers, lakes, and other surface sources and the remainder from wells and boreholes. Of the water distributed to public supply, some (possibly one-third) is used in manufacturing processes. Very much larger volumes, however, are drawn by industry directly from surface or underground sources. Some of this water is used for purposes for which the quality is not of great importance; for example, sea water and brackish water are used for cooling condensers. A considerable and increasing proportion, however, must be of good quality—in some industries it must conform to as rigid a specification as water used for drinking and in a few industries the specification may be even more stringent.

Taken over the whole of Great Britain the volume of water available is more than sufficient to meet the needs of domestic consumers and of industry, though with the growth of large towns and industries it has become necessary in some districts to bring water from long distances and to construct reservoirs in which a reserve can be stored for use during dry periods.

Sources of Pollution

With the growth of population and industry, elaborate precautions have become necessary to prevent the available water from becoming so polluted as to be unsuitable for either domestic or industrial use. Of the water distributed by water undertakers the greater part is finally discharged in the form of sewage. In a residential district this will consist mainly of liquids discharged from water closets, baths, and sinks of private houses, though if a combined system of sewerage is employed it will also include drainage from roofs and roads. Sewage contains coarse suspended matter, colloidal matter, and dissolved substances, mainly of animal or vegetable origin, together

with soil and grit entering with the surface water. In most towns it will also contain a certain proportion of waste waters from industry, including liquors from gas works, laundries, and the like. In an industrial district these trade waste waters may form a substantial proportion of the whole and may greatly alter the character of the sewage. For example, in areas in which there are many woollen mills the sewage may contain so large a proportion of wool grease as to make it profitable to recover it at a sewage-disposal works.

Most of the water taken by industry is used in processes which pollute it to a greater or less extent. The less polluted is usually that used for cooling purposes, particularly for indirect cooling, when the only important effect on the water is to raise its temperature. Most industries, however, include processes which cause profound changes in the water employed. A copper mill may discharge a liquid containing sulphuric acid and copper sulphate. Waste waters from gas works or coke oven plants may contain ammonia, phenolic substances, cyanide, thiocyanate, thiosulphate, and naphthalene. Many industries, including jam making, paper making, manufacture of yeast and alcohol, manufacture of beet sugar, and retting of flax, produce waste waters containing vegetable matter or substances dissolved from vegetable matter or resulting from its decomposition. Another large group of waste waters is discharged from the chemical industries. These may contain acids or alkalis and almost any organic or inorganic substances used in the processes of manufacture. The variety of industrial waste waters is in fact as wide as that of industry itself and the treatment and disposal of these liquids is a problem of the highest importance; most of them must ultimately be discharged to rivers and streams, but at the same time supplies of pure water for domestic and industrial use must be maintained.

Great Britain, no doubt because of the early growth of her industrial system, and the fact that she is densely populated and has only small rivers to provide dilution for polluting liquids, has always been a pioneer in this field. During the nineteenth century and the early part of the twentieth, a number of Commissions of scientific men carried out very important work on which the modern systems of treatment of polluting liquors of all kinds are based. The last and most famous of these Commissions was the Royal Commission on Sewage Disposal which published its final report in 1915. A great deal of research has also been done by water-works authorities, managers and chemists of sewage-disposal works, and industry. Many of the problems, however, can only be attacked

by teams of workers, and in 1927 the Department of Scientific and Industrial Research set up a special Board (the Water Pollution Research Board) to organize investigations on problems of pollution, particularly those of the greatest general interest to the community.

Treatment of Water Supplies

Before discussing the methods which are used to treat polluting liquids it may be of interest to consider what can be done in a modern water works to render a water suitable for domestic supply. Some works draw their raw water directly from flowing streams or from underground sources; others draw from reservoirs in which the water is stored. In the latter case the first problem which arises is to prevent as far as possible the growth of excessive numbers of algæ, which cause trouble in the processes of purification and which when they die may give rise to tastes and thus render the water unpalatable. This problem, which requires the collaboration of algologists and chemists, has been studied extensively—in Great Britain particularly by the Metropolitan Water Board. It is known that a certain amount can be done to check the growth of algæ by the application of such substances as copper sulphate, and that the design of reservoirs and the position of the outlets through which the water is drawn off are important, but the problem has by no means yet been solved.

Many waters, particularly from surface sources, contain material in suspension and this is usually removed either by simple sedimentation or by sedimentation after the addition of such coagulants as aluminium sulphate and sodium aluminate. Here the design of sedimentation tanks is important, and in recent years tanks have been introduced in which the water flows upwards through a blanket of sludge which filters out the suspended particles. Filtration through sand is often used to remove fine suspended matter; this treatment also reduces the numbers of bacteria, and if applied after addition of a suitable coagulant will reduce the colour of water from peaty streams. In the older types of sand filter the rate of filtration was comparatively low and the filters required for a water supply occupied a large area. Modern filters usually operate at a much higher rate of flow per unit area; periodically the flow of water through them is stopped and the suspended matter which has been filtered off is removed by forcing water, and sometimes air, upwards through the bed of sand.

In some districts the water is softened, either by addition of lime or a mixture of lime and sodium carbonate, or by the base-exchange process in which calcium compounds are converted to the

equivalent sodium compounds. Important requirements in water which is to be distributed are that it should not cause excessive corrosion and that it should not deposit large quantities of scale in pipes and fittings. Many natural waters are corrosive and these may be treated—frequently by addition of lime—with the object of bringing about an initial deposition of scale (consisting mainly of calcium carbonate) which will protect metal from further attack. Waters which deposit too much scale are usually treated by softening, but it may be necessary to take further measures to prevent blockage in pipes; addition of sodium hexametaphosphate is one of the methods used.

Finally, if there is any risk that the raw water may be contaminated with pathogenic bacteria it is treated with disinfecting agents. Several methods of disinfection have been adopted; they include treatment with ultra-violet light (not much used in Great Britain), with compounds of silver, with ozone, with chlorine, and very recently with chlorine dioxide. In this country the most usual method is addition of chlorine, sometimes in conjunction with ammonia, which reduces the rate at which the chlorine is subsequently lost from the water. Chlorination is also used to remove certain substances which cause an unpleasant taste; for this purpose it is often necessary to use a comparatively large concentration of chlorine and to remove the excess (for example by addition of sulphur dioxide) before the water enters the distribution system. Another well known way of removing taste is by treatment of the water with activated carbon or other adsorbent material.

Although much can be done in these ways to improve the quality of a polluted water and to render it bacteriologically safe, there is a strict limit to the extent to which it is possible to use a contaminated water to yield a satisfactory public supply. If the water contains large amounts of organic matter discharged into it as constituents of sewage or trade wastes, it may well be impossible to treat it by the methods at present available to yield a safe and palatable product. Waters containing even minute concentrations of certain types of organic substances are particularly difficult to treat; for example, phenol in concentrations which are almost undetectable by chemical means will give rise to noticeable taste when chlorinated. Moreover, a raw water which may at times contain pathogenic bacteria is always potentially dangerous, since there might be a breakdown in the processes of treatment and sterilization which alone can make it safe for drinking. For these reasons great care is taken to protect as far as possible the gathering grounds of waters which are used for public supply, and it may be decided to bring unpolluted water a

long distance to a town rather than to use a near-by source which is known to be heavily contaminated.

Treatment of Sewage

It would be quite impossible to arrange for the distribution of safe supplies of drinking water unless polluting liquors were treated before discharge to streams. Of these liquors the most important, if only because of the great volumes discharged, is domestic sewage.

One of the earliest successful methods of treating sewage was by irrigation on land specially reserved for the purpose. There were many variations in this process. Sometimes sewage was allowed to flow over sloping land; or areas of flat land were flooded and liquid seeping through the top soil was collected in agricultural drains and discharged to ditches and so to a river. It was later recognized that the purification of the sewage depended not only on mechanical filtration, but on the decomposition of organic matter by biological action in the soil, and efforts were made to design plant in which these biological changes could be accelerated. From this work was developed the percolating filter which is now used at the majority of sewage-disposal works in Great Britain. In a modern works of this type the sewage is screened and is passed at a controlled rate of flow through a channel in which grit, washed in from roads, is deposited. It then passes through sedimentation tanks in which other solid matter, largely organic in character, settles out in the form of a sludge; this is removed manually or, in the larger modern installations, by mechanical scrapers.

Disposal of the sludge is one of the difficult problems encountered at a sewage-disposal works. The older system, which is still used at many small works, was to run it on to under-drained beds of graded stone or other material with a layer of sand or ash at the top and to leave it until so much of the water had drained away or had been lost by evaporation that the sludge could be removed with a spade; it was then dug out and very often dumped in another part of the works. It is difficult, however, to de-water raw sewage sludge by this means and many methods of speeding up the process have been tried. One of the most successful, which was developed at the large sewage-disposal works at Birmingham, consists in allowing the raw sludge to undergo anaerobic digestion, when a gas containing about 70 per cent. methane and about 30 per cent. carbon dioxide is evolved; the digested material can be dried on draining beds much more rapidly than the raw sludge. In large modern works the digestion tanks are now heated to maintain a temperature of about 85° F. and sometimes the sludge is stirred during

digestion. The gas evolved represents a valuable asset and is used both for heating the digestion tanks and for driving gas engines, which will usually furnish more than enough power to run the entire sewage-disposal works. At some works in Great Britain during the war, methane obtained in this way was compressed and was used for driving lorries, and it has been used in South Africa for the synthesis of formaldehyde and cyanides.

The liquid from which the sludge has been separated in the sedimentation tanks contains dissolved organic matter as well as much colloidal material. To remove this it is treated in percolating filters which consist of beds, usually about 6 ft. deep, of stone, coke, clinker, or other hard material, carefully graded in size—usually between 1½ in. and 2½ in. The settled sewage is distributed on the filters mechanically, very often by rotating sprinklers driven by the action of the liquid as it is discharged from horizontal jets. The purpose of the filtering medium is to serve as an extended surface to support the micro-organisms which are responsible for the decomposition and oxidation of the organic matter. A filter must be well ventilated at the bottom, since the processes which occur in it are essentially aerobic. The flora is very complex, differing in its detailed composition from one sewage works to another, but it usually consists of an association of bacteria and fungi. Biochemical changes occur very rapidly as the liquid trickles through a filter and comes into contact with the biological film. The time taken for it to pass through the filter varies according to the rate at which it is applied at the surface, but will usually be from perhaps 20 minutes to only 3 or 4 minutes or even less. During this time most of the colloidally dispersed material is removed, the biochemical oxygen demand (that is the proportion of oxygen absorbed from solution in water when the liquid is mixed with water and incubated for 5 days) is reduced from perhaps 25 parts per 100,000 to 1 or 2 parts, and some at least of the ammonia is oxidised to nitrate. The effluent always contains organic matter in suspension, but this—which consists in part of the fæces of worms and other animals—may fairly rapidly be removed by sedimentation.

In addition to the biological film adhering to the filtering medium, a filter also contains a wide variety of other organisms, including worms, springtails, and the larvæ of a number of species of flies. Many of these organisms feed on the biological film, and it is this action which is largely responsible for preventing a filter from becoming overgrown with fungi and bacteria and so becoming choked.

A filter thus contains a balanced community of different types of

organism, supplied with food at a rate much higher than would be the case in a natural habitat. Work is always in progress in an attempt to improve its efficiency—that is to induce it to remove yet greater amounts of organic matter from sewage without either affecting the quality of the treated liquid or causing so great a growth of biological film as to stop the passage of liquid through it. Several new methods of operation have been introduced during recent years. One of these is the process now known as alternating double filtration. In this the liquid is passed first through a percolating filter, then through a sedimentation tank, then through a second filter and a second sedimentation tank. At regular intervals—generally daily—the order of the filters in series is reversed. Trials with large-scale plant have shown that settled sewage can be treated, to yield an effluent of good quality, at a rate per unit volume of filtering medium two or three times that possible with single filtration. The reason is that if a single filter is overloaded the bacteria and fungi grow at a rate which is greater than that at which they can be removed by the fly larvæ, worms, and other scouring organisms. With the high rate of treatment used in alternating double filtration the growth of film on the first filter is very rapid. On alternate days, however, this filter receives not settled sewage, but the effluent from the other filter. This effluent contains little assimilable organic matter and its effect is to cause the masses of fungi and bacteria to disintegrate and so to be washed out of the filter.

Another problem of some practical importance in the operation of filters is that of nuisance from flies. The larvæ of flies (there are several common genera of which *Anisopus* and *Psychoda* are the most important) play an important part in feeding on the biological film, but in the spring and summer the adults sometimes emerge in such numbers as to constitute a public nuisance. No satisfactory methods of biological control have yet been put into practice, but recently considerable success has been achieved experimentally by treating filters with D.D.T. and Gammexane which, when applied in controlled amounts, will kill the larvæ of flies without killing springtails and worms which continue to feed on the biological film.

Another process of treating sewage, which was developed at Manchester, is used at some works. In this the sewage passes first through sedimentation tanks to remove sludge and is then aerated by diffused air or by stirring it mechanically. Particles of "activated sludge" are formed, and these are subsequently removed in further sedimentation tanks and are returned to the aeration tanks in amounts controlled so as to maintain a fixed concentration of activated sludge in the aeration tanks. The structure of

particles of sludge is complex, but it is known that they contain a large proportion of bacterial zoogloeæ, which are mainly responsible for the biochemical changes leading to the decomposition and oxidation of organic matter in the settled sewage. One of the biggest works of this type in the world was built just before the war to treat the sewage from West Middlesex. Some 60 million gallons of sewage are treated daily, the volume of compressed air used being about 50,000 cu. ft. per minute. Nearly 1½ million cu. ft. of gas are obtained daily from the sludge-digestion plant and are used for generating power for heating the buildings and digestion tanks and for operating vehicles.

Treatment of Trade Waste Waters

It has been mentioned that the sewage in some districts contains a high proportion of waste liquors from industrial processes. Discharge into the sewers for treatment with the domestic sewage of a district is usually the most satisfactory way of disposing of these wastes, but is not always possible. There may be no suitable sewerage system accessible or the waste waters may contain substances which would interfere with the treatment of the sewage. For example, some trade waste waters contain substances which inhibit biological activity and would thus reduce the efficiency of percolating filters or of the activated-sludge process. Research is constantly going on to determine the concentrations of such substances which can safely be discharged to the sewers and to find means of removing excessive quantities from industrial wastes. For example chromate, which in very low concentrations inhibits the oxidation of ammonia to nitrate, has frequently to be removed from waste waters before they are discharged from a factory; this may be done by reducing the chromate to chromium salts, which are precipitated as the hydroxide and removed.

The number of types of industrial waste waters treated in percolating filters is always being increased. Not only is this method used for purifying liquids containing most types of organic matter of animal or vegetable origin, such as those from the food industries, but it has also been employed successfully for treating liquids containing substances which would not at first sight appear to be easily amenable to biological attack. Liquors from the manufacture of viscose rayon, which contain mainly sodium polysulphides, are now dealt with in this way, and another waste water containing cresol, ammonia, and formaldehyde, discharged from the processing of phenol-formaldehyde resins, has been treated successfully in semi-scale plant.

The methods used for treating industrial waste waters naturally vary very much with different types of liquor. For some few liquors the only practicable method is evaporation and incineration, and much ingenuity has been devoted to the development of processes for recovering valuable materials from liquors of this type. In the manufacture of alcohol from molasses a mixture of molasses and water to which nutrient salts are added is fermented and the alcohol is distilled off. The residual liquor, which commonly contains about 7 per cent. solids, is very polluting in character and is difficult and expensive to treat by biological methods to yield an effluent suitable for discharge to an inland stream. Many of the methods of disposal which have been proposed, and in some cases worked on a large scale, include concentration of the liquor in multiple-effect evaporators, the concentrated product being used as fertiliser or as food for stock. Other processes which have been used on the Continent include the dry distillation of the concentrate either alone or in admixture with alkalis. Among the products of decomposition are ammonia and amines which have been recovered as such or converted to hydrogen cyanide. Other products which have been recovered include potash, oxalic acid, betaine, and glutamic acid.

Waste waters from some industrial processes are best treated by purely chemical methods. Cyanide, for example, is usually removed from waste waters from electro-plating by precipitation with ferrous sulphate or by treatment with chlorine. Waste washing waters from the pickling of copper can conveniently and often profitably be treated by passing them through a bed of scrap iron to deposit metallic copper; the ferrous sulphate thereby formed is precipitated by addition of lime.

For many liquors, however, the most economical methods of treatment are biological and include anaerobic fermentation, with collection and use of the methane evolved, and aerobic methods such as aeration and biological filtration. In applying these methods to a new type of industrial waste, it is always necessary first to determine the optimum conditions for biological activity, and then to take such measures in the factory as will yield a liquid easily amenable to treatment. It has been shown that the waste waters from the manufacture of paper can be treated biologically, provided that they do not contain too high a concentration of alkali washed from the pulp after the raw materials have been digested with caustic soda; the development of a satisfactory scheme of treatment now depends on improving methods of washing the pulp so that as much as possible of the soda is removed in a comparatively small volume of water; this can then be mixed with the spent soda lye,

which at nearly all mills is concentrated and incinerated for recovery of soda. Waste waters containing high concentrations of organic matter usually have to be diluted before they can be treated satisfactorily by biological methods under aerobic conditions. This is now usually done by using the final effluent from the treatment plant as diluting water, and it is important to ascertain for any particular waste the degree of dilution at which optimum results are obtained.

It has, in fact, been realised during recent years that in developing a method of disposing of an industrial waste it is not generally advisable to start with the liquid which is being discharged from a factory and to develop a method of treating it; a much better solution is usually obtained by first studying in detail the processes which give rise to the various constituents of the waste water and, if necessary, altering the factory processes so as to reduce the volume and strength of the waste produced or to exclude certain constituents of it. In some industries the cost of treating the waste waters produced in the processes of manufacture would be so great that alterations in the factory processes are the only practicable means of tackling the problem. This was the case in the beet sugar industry, where the waste waters from a factory of medium size are equivalent in their polluting effect on a river to the sewage from about 200,000 people. Plant to treat so polluting a liquid would be costly and the solution of the problem has been to reduce the volume of waste waters by re-using the liquors in the factory processes, leaving only a relatively small excess, which can be treated comparatively cheaply by biological means.

Effects of Pollution on Surface Waters

In a healthy and unpolluted stream, oxidation, by bacterial action, of organic matter washed in with the natural drainage is always going on, but unless the quantity of organic matter is unusually high the rate at which oxygen is absorbed in the oxidative processes is no greater than the rate at which it is renewed by solution from the air. This picture is sometimes complicated, in streams containing growing plants, by the diurnal changes in output and intake of oxygen resulting from photosynthesis and respiration. Nevertheless it is true to say that the water of an unpolluted stream is normally substantially saturated with dissolved oxygen, and it is only under these aerobic conditions that the very varied flora and fauna of a clean river are found.

The immediate effect of discharging to a stream sewage or industrial wastes containing large quantities of oxidisable organic matter

is to cause a reduction in the concentration of dissolved oxygen in the water below the point of discharge. If the amount of organic matter added is excessive, conditions may become anaerobic, and methane, hydrogen sulphide, and other products of anaerobic fermentation may be evolved. These changes affect very greatly the organisms, both plants and animals, living in the stream. Marked changes occur, for example, in the species and abundance of algæ. Pollution by organic matter may lead to the growth of "sewage fungus" (a general term applied to a number of species of which *Sphærotilus natans* is the most important), which when it dies and decays usually causes further de-oxygenation of the water and may lead to evolution of hydrogen sulphide. Alterations in the fauna and flora also occur through the deposition of organic mud on the bottom and sides of a stream, the fauna typical of a clean stream giving way to a few bottom-living forms mainly found in mud with a high organic content. Other changes are caused by the discharge of directly toxic substances, such as compounds of copper, which may inhibit bacterial activity and thus delay the decomposition of organic matter and may, in addition, cause profound changes in the composition of the flora and fauna.

It is clear that pollution will have a serious effect on fish life. A fishery may be damaged in many ways—for example, fish may be killed by directly toxic substances, they may be driven away from polluted stretches of a river, they may be asphyxiated if the concentration of dissolved oxygen falls below a critical value (which is higher the higher the temperature), or their food or spawning grounds may be destroyed by deposition of mud. A surprisingly large number of people are interested in the preservation of fisheries, some of which are of considerable economic importance, and much work is done to assess the effect of various polluting substances on them. It happens that the fish of greatest economic importance—the salmon—are migratory and are committed to passing through an estuary during their first journey to the sea as smolts and thereafter during their passage to and from the spawning grounds in the upper reaches of rivers. Estuaries are often the site of manufacturing towns and many British estuaries are badly polluted, with the result that the fish are unable to pass through them and the salmon fisheries are destroyed.

It is often desired to determine the effect which existing pollution of a surface water is having on the quality of the water, on the distribution of plants and animals, and on the suitability of the water for use for some particular purpose, for example for domestic or industrial supply, for navigation, or for a fishery. A common

difficulty in this type of problem is that it is usually impossible to alter during the investigation the volume and composition of the liquids discharged, and the condition of the polluted water, therefore, has to be compared with that of another surface water which is unpolluted but otherwise resembles as nearly as possible the polluted water. An example of an investigation of existing pollution is a survey of the estuary of the River Tees which was carried out some years ago. It was known that the salmon fishery in the Tees had declined almost to vanishing point, and that many salmon were killed in passing through the estuary. One of the chief objects of the investigation was to determine the precise cause of the death of these fish so that the possibility of restoring the fishery could be assessed.

An estuary is a much more complicated system to investigate than is a fresh-water stream. The salinity of the water varies continuously from the head of the estuary to the sea. Moreover, the movement of the water is mainly oscillatory (the amplitude depending on the tidal range which varies from day to day) and superimposed on this system is the seaward flow of fresh water. In the Tees estuary these conditions lead to a pronounced stratification of the water, sea water flowing upstream on the flood tide mainly at the bottom and fresh water flowing seawards mainly at the surface. It is, therefore, difficult to estimate the mean period during which material discharged into an estuary remains in it before passing out to sea. From a consideration of the volume of water in the estuary, the distribution of salinity, and the volume of fresh water entering at the head, it was estimated that the mean period taken to travel through the Tees estuary varied from 3 to 7 days according to the rate of entry of fresh water, and this estimate agreed reasonably well with results of observation of free-drifting floats.

In its central reaches the Tees estuary at the time of the survey was receiving untreated sewage from a population of about 280,000 and waste waters from a number of industries, of which the manufacture of metallurgical coke and the pickling of steel were, as they still are, the most important. Domestic sewage is not directly toxic, and its main effect on a stream arises from its decomposition by biological action, which leads to a depletion of the oxygen dissolved in the water. The industrial wastes contain directly toxic substances and also absorb dissolved oxygen from the water. The rate at which these various polluting substances are oxidised increases with rising temperature ; during the summer in the central reaches of the estuary the concentration of dissolved oxygen fell to 10 per cent. of the saturation value or less, whereas in the coldest

weather the minimum concentration was never much less than 75 per cent. of saturation. Among the chief constituents of the waste waters from recovery of ammonia from coke-oven gas are ammonia, thiocyanate, thiosulphate, cyanide, sulphide, phenolic substances, and tar bases. Although most of these substances are toxic to fish in relatively low concentrations, it was shown (by fractionating samples of the liquors and determining the toxicity of the fractions under laboratory conditions) that toxicity in the estuary was likely to be due mainly to tar acids, of which about 4,000 lb. were discharged daily, and to cyanide, of which the weight discharged was about 1800 lb. CN daily. The problem had thus been narrowed down to that of determining the relative effects of depletion of dissolved oxygen and the presence of the tar acids and cyanide in causing the death of migratory fish. In laboratory experiments, rainbow trout remained unharmed during a month in water with a mean temperature of 15·5° C. and containing dissolved oxygen equivalent to an average of 48 per cent. of the saturation value. Reduction of oxygen to a concentration of 20 per cent. was fatal after short periods; the minimum lethal concentration increased with rise in temperature. Of the direct poisons, cyanide in a concentration of 0·1 part per million was toxic at 6° C. in a relatively short period; the toxicity increased linearly with temperature, being doubled by a rise from 6° to 12° C., but was unaffected by changes in *p*H value between 6 and 8·5. The minimum concentrations of *p*-cresol, phenol, and 1–2–6-xylenol were approximately 4, 6, and 7 parts per million respectively. The toxicity of all these poisons was increased by reduction in the concentration of dissolved oxygen.

Salmon smolts were found dead in the estuary in large numbers between the middle of April and the end of June 1931. During this period water from the central reaches frequently contained toxic concentrations of cyanide, but the concentrations of tar acids were always well below the toxic limit. During the early part of the migration the temperature of the estuary water was about 10° C. and the concentration of dissolved oxygen in the water in which smolts were found dying was from 70 to 75 per cent. of the saturation value; up to the end of May no values of less than 43 per cent. had been recorded. In early June, however, the concentration fell as the temperature of the water rose and values of 20 to 58 per cent. of saturation were found. Thus, during the first part of the migration the concentration of dissolved oxygen was too high to have been directly responsible for the death of fish during the short time they were passing through the estuary,

though at the end of the period the deficiency was sometimes sufficiently great to have caused death. The deficiency throughout the migration was sufficient to increase the toxicity of any directly poisonous substances present.

A series of 283 large samples of water, each taken in duplicate, was examined in the laboratory for toxicity to trout. In one sample of each pair fish were immersed and the period of survival was noted. To the other sample of each pair was added a small quantity of formaldehyde, which by combining with the cyanide to form cyanhydrin destroyed the toxicity of cyanide without affecting the concentration of dissolved oxygen or of tar acids. Of these 283 samples 145 were non-toxic when taken. Addition of formaldehyde produced toxicity in 5 of these samples, 140 remaining non-toxic. In the great majority (130 out of 138) of samples which were toxic untreated, the toxicity was removed by addition of formaldehyde and was thus due to cyanide. This finding was confirmed by observing quantitatively the colour of the gills of smolts found dying in the estuary. The colour was markedly brighter than that of the gills of normal fish, and it had been shown in laboratory experiments that this brightening in colour always occurred when fish were poisoned with cyanide, but did not occur when they were poisoned with tar acids or when they were exposed to water containing low concentrations of dissolved oxygen.

Conditions in the Tees could thus be summed up by saying that the large volume of sewage and industrial waste discharged caused a depletion of the concentration of dissolved oxygen in the central reaches, the extent of the depletion increasing with rise in temperature. In hot weather the estuary would be impassable or nearly impassable to fish by reason of the deficiency of dissolved oxygen alone. During the spring, however, when salmon and sea trout smolts migrated to the sea, the deficiency was not usually sufficient to cause asphyxiation, though it would increase the lethal effect of direct poisons. The mortality was due mainly to the presence of cyanide discharged as a constituent of certain types of waste waters from coke ovens.

The concentration of cyanide in such liquors depends on the details of the process employed for scrubbing the coke-oven gas, and some coke-oven installations discharge only negligible amounts of cyanide. The opportunity for preventing the discharge would come when the coke-oven plants on Tees-side are re-built, and indeed, since the investigation was made one of the largest installations in the world, designed to operate by processes from which there is no discharge of cyanide, has been erected near the mouth of the Tees.

An improvement in the position can, therefore, be expected as older plants are gradually replaced, though if the amounts of sewage and other oxidisable matter discharged are increased the estuary might be rendered impassable during the spring by reason of depletion of dissolved oxygen alone.

Conclusion

In many districts in which industry has been established for a long time the processes of manufacture were designed without there being any information on the effects which would follow from the discharge of the waste waters. The importance of preserving the purity of our remaining unpolluted waters is now well recognised, and when new industries are being planned the question of possible pollution and the steps which may have to be taken to avoid it are usually considered before the details of the manufacturing processes or the exact site of the factory are settled. Frequently the necessary information can only be obtained by the work of teams of chemists, microbiologists, engineers, and hydrographers, with the active collaboration of industry and of water undertakings and sewage-disposal works. Research of this kind is often urgently required at the present time, when so many changes are taking place in the location of towns and industries.

GENES AND DEVELOPMENT

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Of all branches of biology, genetics, the science of heredity, is the most exact, entailing as it does the analysis of an organism into representative units. Geneticists have been able to carry out this analysis because they study the constitution of organisms in their simplest forms, as fertilised eggs. They do not, however, achieve this end by studying the zygote directly ; instead from observation of the adult characteristics of an organism, the phenotype, they have deduced the nature of the genotype : that is, the hereditary constitution of the organism. For the general purpose of studying heredity, the exact relationship between genotype and phenotype has been little investigated. It is only necessary to assume that changes in the genotype produce correlated changes in the adult phenotype. From a wider point of view, the relation between genotype and phenotype assumes a far greater importance. It is the keystone to the whole problem of development.

Development is an historical process, the unrolling of which is controlled by genes, and the whole story can only be told when the actions of the entire set of genes is understood. Between the genotype, defined as the collection of genes brought together in the zygote, and the final adult phenotype lies a complex system of developmental processes. To emphasise the relationship between the causal mechanisms at work during development and the mechanics of the process, which the experimental embryologists have already revealed in part, the term epigenesis has been used. The supporters of the classical theory of epigenesis maintained that development involved the production of something quite new, a complex organism from a simple egg, the stress being laid on the origin of the complex from the simple. The modern interpretation of this theory is that a pre-existing complexity, gene organisation, is manifested in a complexity of a different order, the structure of the animal. With this modification goes the realisation that the final complexity is brought about by the interaction of the constituents of which the zygote is composed. In this sense, which is not exactly the classical one, development may be considered to be epigenetic in character. Furthermore, the use of the term epigenesis lays stress on the dynamic nature of the phenomenon.

The study of the genetics of development, therefore, covers a wide field which has been attacked in recent years from several different standpoints. Fundamentally, it is necessary to discover how a gene works; to reveal, if possible, the chemical and physical reactions which a gene sets in motion, and the mechanism by which this is accomplished. From a different level, the attack can be directed to what a gene does at certain stages of development; how a particular mutant causes the developmental history to differ from the wild type. For the study of genetics is essentially a study of differences. Although this should be self-evident, it is not often realised that it is impossible to recognise a gene unless it exists in at least two forms.

Thus, the method of action of genes during development may be discussed from several points of view. Firstly, it is important to find out how much is known of the substances produced by genes. Work of this type leads naturally to attempts to elucidate the composition and nature of the gene itself, which is a problem outside the range of this article, except where it may have a bearing on developmental reactions.

Very recently, new evidence has accumulated which indicates the correlation between a gene and certain known substances, such as enzymes. The work of Beadle and Tatum (1941) on the ascomycete fungus, *Neurospora*, has demonstrated how the mutation of a single gene can block one step in the life process of the fungus, and from this the deduction follows that the mutated gene is responsible either directly or indirectly, through unknown precursors, for the production of the particular enzyme necessary to complete one step in metabolism. *Neurospora* can be grown on a medium of inorganic salts with a carbon source, such as glucose, and the growth factor biotin. From these it can manufacture all the substances it needs for growth and reproduction. Mutations can be brought about in *Neurospora* by means of X-rays and ultra-violet light, and it is found that some of the mutants produced in this way are unable to live on the usual simple medium which is adequate for the wild type fungus. To discover the reason for this divergence from the normal, vitamins and other substances are added to the medium, one by one, until one is found which enables *Neurospora* to grow. For example, the arginine cycle of *Neurospora* is very similar to that found in Mammals: ornithine is converted into citrulline, then to arginine and thence, by the intervention of the enzyme arginase, to urea. Mutant forms of *Neurospora* have been produced which are unable to synthesise arginine from citrulline, and yet the mutant form differs from the wild type in respect of only one gene. This

gene, in its wild type form, must be responsible for the production of an enzyme which permits the conversion of arginine to citrulline. Similarly, two mutants are known which block the synthesis of citrulline from ornithine ; and other mutants are unable to manufacture ornithine. Of the vitamins, all the B-group, with the exception of riboflavin and folic acid, are necessary in the physiology of the fungus, and mutants have been produced which are unable to synthesise these vitamins. For instance, a mutant strain is known which requires thiamin or thiazole for its normal growth. Another strain which needs thiamin suggests that the mutation has caused a block in the reaction which would normally join the thiazole and the pyrimide halves of the molecule. Again, the synthesis of tryptophane becomes blocked by the production of mutations in the wild type gene complex. From an analysis of the process, it appears that one gene is involved in the production of anthranilic acid and another is responsible for the conversion of the acid to indole, from which tryptophane can be constructed. This suggests that all these genes are concerned with some particular aspect of protein synthesis, either the manufacture of a specific enzyme or the precursor of an enzyme. In parenthesis, it is of interest to record that there are mutant forms of *Neurospora* which do not thrive on the normal growth media and which cannot be made to grow even by the addition of any of the usual chemicals. It must be presumed that in these cases some step in unknown syntheses has been blocked.

Workers (Lindegren, Spiegelman and Lindegren, 1944) on the synthetic properties of yeast have obtained similar results. Thus, the ability to ferment specific sugars such as sucrose, melibiose and raffinose is inherited, and this ability to ferment a given sugar is dependent on the presence or absence of a specific enzyme.

Another point at which genes and chemical substances show a relationship close enough to make it possible to suggest that the former are directly responsible for the production of the latter arises from the study of the blood groups of Vertebrates (Landsteiner, 1936). Blood groups were first discovered in 1900 by Landsteiner and, as a result of further work, it has been shown that human blood can be divided into four groups O, A, B and AB. These symbols denote the presence of a specific agglutinogen, of protein constitution, in the red blood corpuscles. The agglutinogens characteristic of an individual are found to be intimately related to its genetic make up. Indeed, it has been found that agglutinogens are inherited according to simple Mendelian laws. It appears from the evidence that a one-gene to one-agglutinogen relationship

obtains. It is perhaps legitimate to suggest that an agglutinogen, or at least that part of it responsible for its specificity, may be a direct copy of a gene. The same argument holds for other antigens, similar to the agglutinogens, which are found in the blood and tissues of Vertebrates. It has been found that the antigenic difference between any two species is correlated with their systematic divergence determined on morphological grounds. Assuming that, in general, antigens are directly determined by genes, measurements of serological relationships should show the degree of relationship in terms of this particular category of genes.

Other evidence of substances produced by genes comes from the work of Kimball (1942 and 1943) on the Ciliate, *Euplotes patella.* Six separate mating types, the three homozygotes and the three heterozygotes, are known in this organism, and it has been found that culture filtrates from the different types contain specific substances which are responsible for conjugation reactions. An animal may be activated to mate by any of these substances other than the one or two which are specific to, and contained within, itself, a situation very similar to the antigen-antibody relationship. Breeding experiments with *Euplotes* suggest that the so-called "sex-hormones" and genes are directly related.

Examples of this type suggest the possibility of different genes producing substances of very different chemical constitution. So far, there is no direct evidence available to decide this issue, and the only conclusion that can be reached with safety is the rather vague statement that a gene's primary function seems to be to direct the final configurations of protein molecules. Gene reproduction, prior to nuclear division, is of course only a special case of protein synthesis. Thus, assuming that each specific protein of the organism has its unique configuration copied from that of a gene, it should follow that every enzyme, whose specificity depends on a protein, should be subject to modification or inactivation through gene mutation. This has been seen to be the case in the examples quoted above. Tentatively, it may be assumed that the protein copied from the gene is either an enzyme or the precursor of an enzyme. Since all genes appear to reproduce at the same rates, to give an orderly duplication of whole chromosomes during mitosis, the deduction follows that all the genes should produce protein molecules at the same rates. Yet differential production of enzymes appears to take place; that is, some genes work faster or produce more than others. There is no one answer to this seeming contradiction, but there are at least three possible interpretations. It might be that the initial substance produced by the gene is able to increase auto-

catalytically and that different substances increase at different rates in this manner, depending on their chemical constitution. Secondly, the difference may be due to the amount of precursor present in the cytoplasm or, thirdly, it may depend on extra- or intra-cellular substrates.

In a discussion on the rôle of genes in development this survey of the nature of the substances produced by genes may seem to be an unnecessary digression. It is, however, absolutely necessary to consider this chemical aspect of the genes for any understanding of the part which they play in development. If genes are the prime movers in development, they must produce, either directly or through intermediate steps, substances which can set in motion the complex processes which change a zygote into an embryo and thence into an adult organism.

At present, it is impossible to lead smoothly from a discussion of the chemical nature of gene products to the nature of genic action in the production of, for instance, a neurula from a gastrula in a vertebrate embryo. There is as yet a gap between the two types of work, but it is a gap which has been narrowed markedly during the last few years. The experimental embryologists are beginning to supply information which is very suggestive of the type of rôle which can be expected of genes in the early development of animals, particularly of the Vertebrates.

Whilst some authors have cast doubts on the importance of the nucleus, and hence of the genes, in early vertebrate development, it cannot be disputed that, in most cases which have been thoroughly investigated, development for any appreciable time depends on the presence of a nucleus. This does not deny the importance of other considerations, such as cellular movements and the organisation of the cytoplasm of the unfertilised egg. Baltzer, Schönmann, Luthi and Boehringer (1939) have shown that, when Urodeles are hybridised and the female nucleus is then removed, development, with the consequent haploid number of chromosomes, is abortive and usually ceases after the appearance of the lip of the blastopore. Brachet (1945) crossed a female *Triton palmatus* with a male *Salamandra maculosa* and found that development breaks down at the blastula stage, due to a nuclear crisis with the apparition of abnormal mitoses. If part of the epiblast of the hybrid is transplanted to a normal *Triton* embryo, the transplant differentiates normally according to the position into which it is grafted. The host appears to produce a substance necessary for morphogenesis which cannot be made by the hybrids, and the formation of this substance would to depend on the interaction of the nucleus and the cytoplasm

of the same species. Hämmerling (1934) working on the unicellular alga, *Acetabularia*, found that when the cytoplasm was deprived of its nucleus it retained its capacity to perform physiological functions, but could not undergo regeneration. It could respire and metabolise in order to carry on the day-to-day functions of life, but was incapable of manufacturing new proteins for its body substance.

Having established the necessity for the presence of genes in normal development, the next step is to find out, if possible, how they intervene in this process.

Latterly, the activity of genes has come to be associated with the presence of nucleic acid on the chromosomes, and with the possibility of the presence of nucleic acid of a different constitution in the cytoplasm. In 1910, Masing verified Loeb's hypothesis on the amount of nucleic acid present in the egg of a sea urchin. He compared the virgin sea urchin egg with the blastula stage and found that the total amount of nucleic acid was the same, whether one or one thousand nuclei were present. Yet, cytologically, the nuclear content of nucleic acid increases visibly during this time. The virgin sea urchin egg gives only a slight Feulgen reaction, that is, a reaction indicating the presence of desoxyribose, or thymo-nucleic acid, localised on the chromatin, and the inevitable conclusion seems to be that there must be in this egg another nucleic acid which does not give a Feulgen reaction. During the course of segmentation, the cytoplasm adjacent to the resting nucleus takes up toluidine blue, an indication that these regions are exceptionally rich in the nucleic acid recognised as ribose nucleic acid. Further work has shown that the nucleic acid of the virgin egg is largely in the form of ribose nucleic acid, scattered through the cytoplasm, and that, as segmentation proceeds, the ribose nucleic acid becomes converted into desoxyribose nucleic acid situated in the nucleus, thereby altering not the amount of nucleic acid, but its distribution. We know practically nothing of the change from ribose to desoxyribose nucleic acid, but the transformation may not be a direct one.

Brachet (1940) and Caspersson (1939–40) have shown that ribose nucleic acid is found abundantly in the cytoplasm of pancreatic cells, the Nissl granules of nerve cells, in young oocytes, cells undergoing active proliferation and also in the nucleoli. In fact, there exists a close relationship between the amount of ribose nucleic acid in a cell and its ability to perform protein synthesis (Caspersson *et al.*, 1941). It seems likely that the ribose nucleoproteins of the cytoplasm are responsible for the synthesis of the cytoplasmic proteins.

This remark, standing alone, gives little indication of the con-

nection between protein synthesis and the genes. During the last few years, however, a great deal of attention has been paid to the structure of the chromosomes during cell division and during the so-called resting stage. It appears, from the work of many authors (Koltzoff, 1928; Signer, Caspersson and Hammarsten, 1938; Schultz, 1941) that the chromosomes consist of a protein framework to which is attached, by chemical combination, varying amounts of highly polymerised desoxyribose nucleic acid. The nucleic acid is at its maximum density on the chromosomes during nuclear divisions, increasing visibly in the early stages of mitosis and meiosis, and decreasing again during anaphase and telophase. As the desoxyribose nucleic acid content of the chromosomes increases, there is a concomitant decrease in the amount of ribose nucleic acid in the cell as a whole. This suggests that one form of nucleic acid can be converted into the other, a possibility that has already been noted above.

The chromosomes are not homogeneous in substance, but have been shown to be made up of euchromatic and heterochromatic regions. The euchromatic regions have been identified with the genetically active areas, and here the protein framework may be of a protamine type, whilst the heterochromatic regions may be histone in structure (Caspersson, 1940) and are usually considered to be genetically inert (Heitz, 1933). During the resting stage, the heterochromatic regions retain more nucleic acid than do the euchromatic parts. It has been shown, notably by Brachet (1942), that the chromosomes do not contain only desoxyribose nucleic acid, but, in addition to large quantities of it, a small amount of ribose nucleic acid is found in the heterochromatic regions. The other nuclear structure of particular interest in the present discussion is the nucleolus. Caspersson (1941) has shown that the nucleoli are rich in ribose nucleic acid, and that there exists a relationship between the presence of large nucleoli and the amount of nucleoprotein in the cytoplasm. Nucleoli are well developed in growing oocytes, nerve cells, gland cells, cancer cells and embryonic cells, while absent from those cells, such as leucocytes, which do not synthesise proteins.

There is, therefore, ribose nucleic acid in the cytoplasm and the nucleoli of cells engaged in protein synthesis and desoxyribose nucleic acid, and a minute amount of ribose nucleic acid, on chromosomes which are reproducing. Caspersson and Schultz consider that it is the heterochromatin which is the region of the chromosomes which controls the synthesis of nucleic acids. The tentative conclusions to be drawn from all these observations is that the

nucleic acids of the cytoplasm and the nucleolus play the parts of intermediaries between the heterochromatic regions of the chromosomes and the proteins of the cytoplasm.

Another line of work brings evidence of the presence of ribose nucleic acid in the cytoplasm. Claude (1938–40) showed that, when a bird tumour is ultracentrifuged, small particles are seen, with the aid of an ultramicroscope, and the particles consist of ribose nucleoproteins and are infectious. Stern (1939) showed the presence of similar granules in cardiac muscle, and Brachet and Jeener (1945) have obtained them from diverse vertebrate organs, from Invertebrates and from yeast cells. Their abundance is directly proportional to the amount of ribose nucleic acid in the organ, calculated by different methods. In fact, in adult organs practically all the ribose nucleic acid appears to be associated with these "granules," whilst in the amphibian egg Brachet and Chantrenne (1942) found that the "granules" contain only 20–40 per cent. of the total ribose nucleic acid content, the remainder being found free in the cytoplasm. Associated with these "granules" are found peroxidases, indophenoloxidase and various other enzymes such as phosphatase, amylase, ribonuclease, cytochromoxidase and succinodehydrogenase. These "granules," therefore, would be an ideal site for protein synthesis, containing as they do all the necessary enzymes for the assurance of oxygen, etc. The close connection between the presence of ribose nucleic acid and the manufacture of the cytoplasmic proteins makes it appear very likely that the nucleic acid is concerned in protein synthesis. This supposition is strenthened by what has already been seen of the work on *Neurospora*, but as yet there is no very good evidence of the exact nature of the reactions which are involved. Chantrenne (1945) has suggested that the nucleic acid precipitates the products of synthesis of the proteases, so that the enzyme equilibrium would be constantly shifted in the direction of more synthesis. But this is no more than a speculation.

The evidence then indicates that the nucleus is necessary for normal development, in that it is concerned in protein synthesis, and that it is the ribose nucleic acid, which has been proved to occur in the cytoplasm of active cells, which is in some way involved in this protein synthesis.

So far in the discussion, the developing zygote has only been permitted to make proteins, and the whole question of how a zygote is organised into an embryo and finally into an adult has yet to be considered. In what way are the genes concerned in the fundamental processes of evocation and induction ?

It has been known for a long time that all manner of substances will cause evocation in vertebrate embryos, substances as far apart as broken glass and sterols. Methylene blue and thiols will cause neuralisation of ectoblast tissue ; and it has been shown that it is sufficient to kill a portion of epiblast to make it take on inducing powers which it did not normally possess. In fact, active substances of induction are widespread : abundant in Vertebrates, less so in Invertebrates, and recently proved to be present in plants and yeast.

Fischer *et al.* (1935) showed that nucleoproteins of thymus, pancreas and liver are very good inducers even after they have been purified and separated from the lipides which might contaminate them. They are, however, only effective if injected directly ; carrying them in agar immediately reduces their efficacy. At much the same time workers in Cambridge (Waddington and Needham, 1935) had reached the conclusion that a sterol was the responsible agent of induction. Induction by regions of killed gastrula tissue, by sterols, dyes and nucleoproteins must, in some way, be reconciled.

It seems that most of these agents may bring about a denaturing of proteins, which inevitably leads to a rise in the proportion of —SH groups. Sterols and acids, which are catalysing agents, might well provoke such a denaturing and subsequent increase in —SH groups. Holtfreter (1934) has shown that young oocytes of Batrachians are better evocators than older ones and that these young cells contain more —SH groups than the older ones. But, if it is —SH groups which are responsible for evocation, it is peculiar that substances such as coagulated white of egg, cystein and glutathion have proved useless as evocating agents. Brachet and Rapkine (1939), on the other hand, have shown that blocking of the —SH groups does not cause any disappearance of evocating ability. In embryos where the —SH groups have been blocked by iodoacetamide or chloropicrine, a notochord is formed and normal somites, but the nervous system remains rudimentary and often incompletely closed. The —SH groups appear to play some part in the normal development of the nervous system, but they are clearly only part of the story. It has been shown that proteins rich in —SH groups, found in the eggs of Amphibians, are closely associated, from both a morphological and a biochemical point of view, with nucleic acid. If it is the nucleic acid which is the active principle, rather than the —SH groups, this would explain why white of egg and glutathion are of no use as evocating agents, for they do not contain nucleic acid. To investigate this possibility,

Brachet (1942) has worked on the correlation of nucleic acid with morphogenetic potentiality. He found, for instance, that heat treatment, which killed the inducing agent, also removed the ribose nucleic acid. In fact, the resistance to heat of nucleoproteins and of inducing agents proved to be identical. He also implanted fragments of dead tissue which had been deprived of their ribose nucleic acid, by treatment with ribonuclease, into other amphibian embryos and found that the number of inductions fell significantly from 60 per cent. in the controls to 20 per cent. in the treated embryos. With pure ribose nucleic acid, the experiment was even more dramatic, the number of inductions falling from 45 per cent. with the pure acid to 0 with the treated acid. Presumably in the first experiment there was a certain amount of contamination of the acid which would account for the few inductions which were produced.

It has been known for a long time that the pronephros of Amniotes never forms a functional kidney, but that it is essential for the formation of the later kidney, inasmuch as it functions as an inducing agent. The pronephros possesses morphogenetic properties which are intermediate in power between those of the somitic mesoderm and those of the lateral plate mesoderm. Recently (Yamada, 1939), it has been shown that the pronephros occupies this same intermediate position in respect of its ribose nucleoprotein content.

It seems that dead tissues owe their evocating power to their ribose nucleic acid, but that, when they are implanted into the host, they only gain evocating activity when the nucleic acids have been attacked by that host. For instance, in 62 *Discoglossus* embryos, not one case of induction was found without a fall in the content of the nucleic acid of the graft being recorded (Brachet, 1945). This evidence, taken with that of Fischer and his colleagues, brings the nucleic acids to the fore in yet another light. Ribose nucleic acid forms some part of the evocator-inducing process which brings about the normal development of an embryo, and ribose nucleic acid is associated with the desoxyribose nucleic acid of the chromosomes. It is probable that it is not the ribose nucleic acid itself which induces the formation of a nervous system, but, more probably, the acid is hydrolysed under the action of the host ribose nucleases, and it is the simple nucleotides, which are released in consequence and, being soluble, might be the causative agents.

To sum up the preceding paragraphs, most cases of evocation by miscellaneous substances can be accounted for on the basis of hydrolysis of the nucleic acids. The nucleotides, formed in this

way, intervene in the synthesis of ribose nucleoproteins, and these in turn elaborate new proteins, and an organ is formed.

Since ribose nucleic acid appears to play a fundamental part in morphogenesis, it may be that the short and abortive development of amphibian larvæ, deprived of a set of chromosomes, is due to the inhibition of the synthesis of ribose nucleoproteins. Hybrids, produced as described above and examined for nucleic acid content, show that, at the time when development ceases, the synthesis of ribose nucleic acid has also ceased. This synthesis becomes normal again, as does the development, when a portion of the abnormal larva is grafted into a normal host. For Invertebrates, Caspersson and Schultz (1938) have shown that the synthesis of ribose nucleoproteins in the oocyte of *Drosophila* is conditioned by the constitution of the nuclear chromosomes.

At this point the problems of cellular differentiation may be mentioned briefly. The ribose nucleic acid content of a cell increases rapidly in each organ as it forms and subsequently diminishes when cytological differentiation is complete. For instance, the notochord increases rapidly in nucleic acid content during its formation and then loses its acid when the cells become vacuolated. Organogenesis proceeds hand in hand with the synthesis of ribose nucleoproteins, probably connected with the production of specific proteins. When differentiation is complete, the ribose nucleic acid disappears and the proteins characteristic of each organ have been made and the synthesis slows down. A study of the "granules" isolated from different adult organs shows them to be chemically and serologically distinct, which suggests the further possibility that these sites of ribose nucleic acid activity become modified in the course of development. Thus, the specificity of cells and tissues probably depends on their content of specific proteins which are laid down under the influence of ribose nucleoproteins during organogenesis. There is as yet no direct evidence of the prime cause of this protein specificity or of "granule" specificity.

The net result of the work of the experimental embryologists on the very early stages of development shows, therefore, that genes are able to bring about certain fundamental changes, such as evocation or individuation through the activity of ribose nucleic acid, which is located in the cytoplasm and manufactured in some way from the desoxyribose nucleic acid characteristic of the chromosomes. No work has yet been done on the effect of introducing mutant genes and studying the differences which they cause in normal development at this early stage of vertebrate embryology. The subject has not reached a stage of such precision. It merely

demonstrates the way in which the nucleus, or the whole gene complex, sets about its general task of producing a normal embryo.

Such a comparative study of genes and development has been carried out by other workers in recent years. The attack has been on a rather different level from that of the experimental embryologists. Mutant genes have been introduced, one by one, into an otherwise wild type complex and the developmental differences between the two have been studied. The mutants studied in this way have been those whose effects become apparent at a comparatively late stage in ontogeny and whose effects are on one or a few organs of an animal or plant. By studying such late acting genes, the developmental pattern is only slightly altered and the organism reaches maturity. As more is known of the effects of these comparatively superficial mutants, the study will presumably be pushed back to the earlier stages of development to meet the problems of the experimental embryologists.

Attacks from this angle have been made by many workers, particularly on the development of the eye pigments in normal and mutant forms of *Drosophila*, and also on the colours of flowering plants. Experiments by several authors, notably Ephrussi (1938 and 1942) and Beadle (1939) have revealed a complex chain of chemical events leading to the production of the normal red eye in the wild type *Drosophila melanogaster*. Before the synthesis of the red pigment can start, it has been shown that the substance tryptophane must be present in the body of the animal. Recent work (Tatum and Haagen-Smit, 1941) suggests that this initial requisite is obtained, for the most part, from the food on which the larva feeds. The tryptophane becomes changed, by the action of the wild type allelomorph of vermilion into α-oxytryptophane and thence to kynurenine, the vermilion substance. Once more it must be stressed that the only reason for supposing the existence of a gene is the fact that it may exist in more than one form, and this is well brought out in a study of eye pigments. There is no specific name for the wild type gene which gives rise to kynurenine, and its existence would not be known if it did not have a mutant allelomorph vermilion which alters the course of development of the pigmentation. The result is that the indication of the existence of such a gene can only be given by the rather cumbrous phrase, wild type allelomorph of vermilion, denoted by the symbol v^+. The kynurenine, or v^+ substance, is diffusible throughout the body of the larva and pupa, but it must be absorbed before the seventieth hour after pupation. This diffusibility has been demonstrated by injection of lymph from larva to larva, and also by the technique

of transplantation between larvæ, which has proved to be an invaluable method for the study of certain genetic effects (Ephrussi and Beadle, 1936). For instance, the gonads of the larvæ are comparatively easily distinguished and are unattached to ducts during their larval period. The gonad alone can, therefore, be removed from the larva and transplanted into a new host. During pupal life the transplanted gonad makes connections with the gonadal ducts, and a fairly high proportion of the operated animals survives to maturity. Thus, flies can be produced whose gonads differ from the soma in respect of one or more known genes. Other organ rudiments, such as eye discs, can also be transplanted in this way.

Having established the part played by the v^+ gene in the development of the normal eye, it should be remembered that if, instead of the wild type allelomorph of vermilion, the vermilion mutant itself is present, the eye pigmentation follows the path leading to the production of vermilion eyes and not to the wild type colouring.

The next gene to be concerned in the process is the wild allelomorph of cinnabar, the cn^+ gene. The presence of this gene causes the kynurenine to be converted into a chromogen, the cn^+ substance. It can be shown, by transplantation of eye discs from one host to another, that the substance formed by the cn^+ gene is of a kind that will permeate the body of the organism. The chromogen then becomes converted to the definitive red pigment by the activity of the wild type allelomorph of brown. All that is known of the nature of the red pigment is that it is of low molecular weight, probably forming a protein complex, and that it shows *p*H and oxidation-reduction colour changes. Other gene-controlled reactions must contribute to the sequence leading to brown pigmentation. It is known that the production of this pigment cannot be brought about if either the scarlet or the cardinal wild type genes are not present. The chemistry of the production of this brown pigment is not yet understood, but it does appear to be manufactured from the cn^+ substance, as has been seen to be the case in normal red eyes. The scarlet and cardinal wild type genes must intervene after the functioning of the cn^+ substance, because flies of both mutant types produce both kynurenine and cn^+ substances.

Although this pigmentation is strictly confined to one organ, the insect's eye, the precursors of the final pigment are, in fact, diffused throughout the organism during its early developmental history. Even so, it must be realised that the final effect is a strictly localised one: the production of red pigment in the eye

and in the eye alone. To convert the precursors into definitive pigment in one place only, there must be a dependence on some local reactivity of the organ, and this reactivity must ultimately be itself under the control of genes. There must, therefore, be genes whose effects are strictly localised, though it is difficult, at present, to see which these genes are. This example shows clearly the correlation between one gene and the production of a specific chemical substance which was discussed earlier.

Many workers (Lawrence, Scott-Moncrieff and Sturgess, 1939; Robinson and Robinson, 1939) have shown a similar correlation between the activities of genes and the production of specific substances in studies on the colouring of flowering plants. Most of the water-soluble red, blue and yellow pigments found in flowers are anthocyanins or related compounds. In the sweet pea, *Lathyrus odoratus*, the pigmentation is dependent on the presence or absence of anthocyanins and anthoxanthins. It has been found that two complementary dominant genes are necessary for the production of anthoxanthins in this plant. If either of the genes is present in a homozygous recessive form, no anthoxanthin is manufactured. For instance, the genes called copper and maroon suppress all the anthoxanthin production, without, however, inhibiting the manufacture of anthocyanins. Similarly, the presence of anthocyanins is dependent on two complementary factors, and the genes mauve and picotée reduce the amount of anthocyanin, whilst allowing an increase in the amount of anthoxanthin. Robinson postulates that both anthocyanins and anthoxanthins have a common origin. It is an observed fact that there exists an inverse quantitative relationship between anthoxanthin and anthocyanin pigment types. If one is increased through gene substitution, the other is observed to decrease. Modifications of the anthocyanins, once they have been produced, can be brought about in a variety of ways, dependent on the genotype of the individual plant. For instance, anthocyanins are *p*H indicators and the acidity of the cell sap is under the control of genes. In all cases, more acid cell sap is dominant to the less acid condition. This difference of *p*H is of the order of one-half to one *p*H unit, and it is interesting to find that the change in acidity is strictly localised within the petals, a condition analogous to the local production of pigment in the eye of *Drosophila*. Work in this field seems to support rather strongly the hypothesis that each gene functions primarily in the control of one specific chemical reaction.

The implications of the last two examples will be apparent. The activity of a particular gene depends on its relationship with

all the other genes which go to make up an organism. The spatial inter-relationship has been stressed many times. It is the gene complex which is of paramount importance, not any particular gene considered in isolation. The study of developmental effects has brought out very forcefully the temporal relationships which are involved in the production of a definitive adult. The working of any particular gene will depend, not only on its spatial relationships with the other genes, but also on its position in the time sequence of development. The gene will only be able to work within the framework imposed on it by what has gone before, and on what it does will depend the workings of those genes which come into action at a later date.

A very beautiful example of the far-reaching effects of one gene which comes into action early in development has been described by Grüneberg (1938) in mice. One gene, the "grey-lethal," brings about a lack of yellow pigment in the fur and a failure of the absorption of bone, which is the normal accompaniment of growth. This failure of bone absorption involves a whole set of secondary consequences. The minerals of the body are rendered immobile, locked up in the bones, and cannot, therefore, be used for growth in the normal way. As a result of this, the teeth are incompletely calcified and unable to masticate solid food. Lack of bone absorption also leads to pressure on some of the nerves, particularly those of the lower jaw, and this interferes with the normal suckling reactions, so that the animals show less inclination to take milk from the mother than the normal. The "grey-lethal" mice, therefore, show signs of starvation, and the animals die either before weaning, through lack of milk intake, or, if they survive this period, they die as a result of starvation due to their inability to eat solid food. The network of the gene complex has been disturbed by one gene at an early stage of ontogeny, and this instance illustrates the far-reaching effects which such a disturbance may have in the subsequent development of the animal.

On the other side, there is the study of one organ and the many genes which affect it, as has already been seen in the brief description of eye pigmentation. This was largely the transformation of one type of chemical substance into another, but there are other examples, in which the action of a gene cannot be so closely tied with a chemical reaction, but which do throw light on the effects of genes in development, and are, therefore, worth considering in some detail.

The first step is to describe what can actually be seen during the normal development of the organ under consideration, and then

to study the divergences from the normal which occur when a particular mutant gene is substituted for the normal. Wing development in *Drosophila* has been subjected to just such a minute analysis (Auerbach, 1936; Dobzhansky, 1929; Goldschmidt, 1935; Waddington, 1940). During the normal development of the wing, the first visible sign of a rudiment is that of the imaginal wing bud which can be seen near the dorsal surface of the larva. During the last larval instar, these buds become folded and form into hollow sacs. At this juncture the larva becomes quiescent and develops a puparium, or hard skin, around itself, and it is during this apparently inactive period that most of the wing development takes place. The wing sac becomes everted, as though the finger of a glove were turned inside out, and the wing surfaces come to lie close together, except for a few hollow spaces in which the blood lacunæ run. Following this, the whole surface of the wing expands. This expansion is brought about by an actual change in shape of the cells, all the cells becoming flat instead of rather cubical in shape. At the same time, the cells divide rapidly to give an increase in the whole surface area. If a study is made of the development of the wing in a *Drosophila* which bears in its gene complex the mutant gene for narrow wings, it is found that it is at this point in ontogeny that the normal processes are modified. In fact, the cells of the wing divide more rapidly in the direction parallel with the long axis of the wing than they do in a transverse direction. Conversely, the mutant gene for broad wings causes the cells to divide more rapidly across the long axis than parallel with it. Once this differential cell division has taken place, the wing is, as it were, committed to taking on a narrower or broader form than is usual.

Next, chitin is formed on the wing, chiefly round the edges, and then the whole wing contracts slightly, and the blood lacunae, which are now visible, are the first appearance of the sites of the final wing veins. The longitudinal veins are formed first, and later the cross veins can be seen as the last vestiges of the wing cavity. There is a mutant gene known as cross-veinless, whose effect is to produce a definitive wing in which the posterior cross vein is absent. A study of the development of an individual bearing the gene cross-veinless shows that, instead of the last cavities persisting after the long veins have been formed, the central cavity, which might be expected to become the posterior cross vein, vanishes at this stage. It can be said, therefore, that at this moment, about 30 hours after the formation of the puparium, the genetic make-up of the individual determines whether it will be

with or without the cross vein. The sensitive period, that is the period during which a gene can exert its influence, of the two mutants narrow and cross-veinless is very different, a matter of about 20 hours.

Following on the formation of the definitive veins, the wing expands again, by an enlargement of the cells, probably due to the taking in of a quantity of water, and the adult chitin is laid down. Now, as the wing expands, it sometimes happens that small cavities persist in various parts of the wing, and chitin is laid down where the cavities persist, so that a fly emerges with extra bits of vein material. This condition has been given the name of plexus and it is exactly this persistence of cavities which comes about in individuals bearing the gene for plexus.

Finally, the adult fly emerges from the pupal state and, when it does so, its wings are at first folded and damp. The internal pressure and the movements of the body cause the fluids from the wing to be withdrawn and the wing dries out and unfolds. This normally gives rise to a straight, flat wing, but if the individual bears the mutant gene for Curly the wing does not dry out into a flat plate. Instead, an undue contraction of the upper surface causes the wings to become curled upwards. The opposite holds true for the mutant curved, in which the wings curve downwards over the body.

During the first 48 hours of pupal life, the wings undergo at least fifteen different processes, of which only a very few examples have been sketched in here. Each process has been shown to be affected by some known gene. Each gene has its place in the spatio-temporal network, which causes the development of an organ, in this case, a wing.

These natural experiments, or observations, have been checked by experiments of a more conventional kind. A series of operations has been performed on the developing wing by Lees (1941) using fine glass needles. Operations at an early stage after pupation (3–6 hours) produce very characteristic round, short wings. The operation proves to have inhibited the cell multiplication which normally takes place at this time, and this upsets the differential growth rates of the cells. This cell multiplication was shown in the earlier observations to be the cause of a change in the proportions of the wing.

Other confirmatory evidence comes from the work of Sung-Yün Ma (1943) on the effects of temperature shocks on the pupae of *Drosophila*. Normal *Drosophila* pupae, submitted to a high temperature, 40° C., for about 2 hours do not all achieve normal

development. A certain proportion of flies, with a wild type genotype, emerge with narrow, cross-veinless or plexus wings and many other variations. This effect simulates the effect of a mutant gene and is known technically as a phenocopy. The changes brought about in this way are not mutations, for they are not inherited. The result of such treatment depends on the time at which the pupae are heated. In the early hours of development, around 10 hours after puparium formation, treatment results in a few flies with narrow or broad wings. Pupae treated later in life give rise to a certain number of adults with plexate wings, but never to flies with narrow or broad wings. It is apparently too late at this stage to affect the cell divisions. The time at which the maximum number of narrow wings appears, by means of this treatment, is the time at which cell division and expansion is taking place. Presumably the high temperature causes differential cell division or expansion of the wing cells, as was seen to be the case with flies carrying the mutant gene for narrow.

As another example, consider the genes in *Drosophila* which affect the development of the bristles on the thorax (Lees and Waddington, 1942). The first stage of normal bristle production is concerned with the determination of the bristle cell. Some time during pupation, cells are set aside which will form the bristles and their sockets. These cells divide to give trichogen cells which will secrete the bristles themselves, and the tormogen cells, which form the sockets round the bristles. The trichogen cell lies under the tormogen cell when the two come to lie near the surface of the epithelium. The cells are difficult to identify before 21 hours after puparium formation, although by 30 hours the bristle is already distinguishable and its growth is completed by 55 hours.

If the gene for split bristles is introduced into the gene complex, the normal process is modified during the early stages. Chronologically, the first process to be affected is the division of the cells set aside for bristle production. Some time before 16 hours after pupation (the exact time has not yet been determined) both the tormogen and trichogen cells undergo an extra division, to give groups of four, instead of two, cells. In some cases, these four cells may lie rather further below the surface of the epithelium than is usual, in which case they remain small and do not secrete either bristle or socket. In other cases, they may arrive at the surface normally and two secrete bristles and two form sockets, so that two bristles, complete with sockets, appear in the adult in a position normally occupied by only one. The next important step in bristle production is the arrangement of the trichogen and tormo-

gen cells in relation to one another. Normally, the trichogen cell lies under the tormogen cell, but in split, as a result of abnormal arrangement, one bristle and a socket made up of three parts may appear. One only of the four cells has become a bristle producer, whilst the other three have presumably come to lie above this cell and manufactured sockets which coalesce to give one tripartite structure. To determine the sensitive period for split, that is the time period within which the extra division must take place, the temperature shock method can be used. It appears that this division takes place usually in the very early hours of pupation and that after 21 hours the sensitive period is over. In other words, during this time, an abnormal environment may cause an extra division, with the consequent different developmental sequence. Once this division has occurred, the line of development is predetermined within certain limits: any number of other factors may alter the size or shape of the bristles, but the path towards a double, or split bristle has been chosen irrevocably.

The next stage in normal bristle formation is the enlargement of the trichogen cell. It becomes very large by the accumulation of cytoplasm within itself, which is eventually pushed out of the cell as a bristle, whilst the tormogen cell secretes a socket round it.

The growth of the bristle is, as would be expected, under the control of genes, and several mutants are known which alter the growth rate at this juncture. In the mutant spineless, both the large bristles (macrochætæ) and the small ones (microchætæ) are very much reduced in size. This appears to be a simple effect on the growth rate of the bristle-forming cells. They fail to increase their cytoplasmic content at the normal rate and, as they start secreting the bristle at the usual time, the bristles are considerably smaller than those of the wild type. The growth of the trichogen cell is followed by the actual secretion of the bristle, and the tormogen cell secretes the socket around it. Normally, the bristle secreted in this way is quite straight and tapers to a point. Several genes are known which affect the secretion of the bristle, notably the gene forked. Forked bristles are fatter and shorter than the normal and are bent and split at the ends to a marked degree. Histological studies show that the developing bristles appear quite normal until some time after the secretion of the bristle has begun. After growing for about half their length, the bristles start curving round and splitting. It has been suggested (Lees and Picken, 1945) that the forked shape of the bristle is caused by a sharp initial rise in the cytoplasmic synthesis which leads to a fatter rudiment than normal. In addition, it appears that the mechanical properties

of the bristle walls are altered so that they become more plastic than usual, allowing for the splitting and bending of the ends.

The last stage in the production of the definitive bristle is a darkening and hardening process. The introduction of a gene such as straw prevents this darkening process and the bristles appear very pale yellow in colour.

Thus, a gene functioning early in pupal life may have an effect on the cell-division of bristle-forming cells. Should an extra cell-division take place, no amount of subsequent normality will return the bristle to an exactly normal type. Later, when the trichogen cell has become differentiated, a gene is able to exert its influence by changing the bristle development path to produce differently shaped bristles, and still later, genes (and temperature shocks) can give rise to unpigmented bristles.

The results of the temperature shocks, taken in conjunction with the descriptive work on the development of individual organs, confirm the time at which a particular developmental process takes place and also indicate the period of time during which, for instance, cell multiplication can take place. Extensive study of temperature shocks suggests that effects can sometimes be produced which simulate a known mutant, but which cannot be attributed to the same developmental effect, since the sensitive period proves to be different from that of the time of action of the gene. The way in which this is brought about is not at present clear.

This leads to another piece of experimental work, designed to show the interaction of gene effects, more particularly the effect which a gene can exert when confronted with an abnormal situation.

The antenna of *Drosophila* consists of a small basal joint, a swollen second joint and a third joint bearing the arista, a tapering chitinous spike bearing numerous branches. The recessive mutation aristopedia, ss^a, causes the arista to be transformed into a leg-like organ, of several joints terminating in a typical tarsal claw. There are, therefore, two alternative ways in which the antennal disc can develop, into either an antenna or a leg. At some moment in development, the path, down which development shall proceed, is determined: whether an antenna will be produced or a leg. This is, of course, only a more dramatic instance of what has already been seen in the foregoing examples. At definite moments in the course of development, the organism is confronted with alternative modes of development, and the gene which the organism possesses switches the development down one path or the other. Later, developmental effects can take place only within the limits set by preceding genes. A wing which has taken the path towards

narrowness will remain narrow, although it may become plexate and cross-veinless in addition. *Drosophila*, from which the vermilion wild type allelomorph is absent, will proceed down the path towards vermilion eyes.

What, however, will be the effect of introducing into an aristopedia stock genes which normally affect the legs and not the antennæ? What can be learnt of the interaction of such genes? Aristopedia has been combined with genes affecting the tarsi, such as dachs and four-jointed (Waddington, 1940). Four-jointed, as its name implies, reduces the number of joints in the leg from five to four. A four-jointed aristopedia fly has a shortened aristal tarsus and the number of joints is reduced. Thus, when the antennal disc follows the tarsus-like developmental track, it is affected by the tarsus-affecting genes. These genes help to define the path which has already been determined, although they have no effect on the track leading to the development of a normal arista. They appear, therefore, only to be able to react with an organ which is developing along a particular course, in this case towards a leg.

During the short history of genetics, and for that matter of evolution also, the adult animal has had a blinding influence or has, at least, directed studies into certain circumscribed channels. Genetics has been a study of statics or, in other words, of phenotypes, and genotypes only by assumption. The general trend in biological thought in more recent years has been towards the study of the dynamics of certain phenomena, to ask how a thing works in addition to why it works. The study of genes and development is a very clear example of this swing over to a search for the processes involved in the production of an individual rather than to the enunciation of the differences and similarities between adults. For many years, the experimental embryologists have worked mainly on the very early stages of development, and the geneticists on the adult phenotype, and a yawning void has existed between the two. It is self-evident that the two have a great deal to contribute to one another for their mutual benefit, and at last the gap is closing, and closing rapidly. The workings of the gene complex are inextricably tied up with interpretations of development, for without genes development does not take place. The examples that have been cited show clearly that there are no developmental effects which are not ultimately controlled by genes. To discover how a gene exerts its controlling influence it is necessary to inquire into the nature of the substances produced by genes. From there the effects of these products must be elucidated, for example the exact nature of the evocating and inducing agents. This study, in

the field of the experimental embryologist, is beginning to give a picture of the very early effects of genes, the broad and fundamental processes which set a zygote on the right road to become an embryo and, subsequently, an adult. From there the geneticist takes up the story to discover what genes do in organogeny and how mutants differ from their wild type allelomorphs. Every stage from the early segmentation to the final elaboration of a pigment within the limited space of a *Drosophila* eye is controlled by genes. Genes do not just pop in now and then during ontogeny; they are essential to the orderly workings of the whole process. There are still many gaps, but the experimental embryologists and geneticists, working together on similar problems at different levels of development can now express more than a pious hope that their work will one day coincide.

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MODERN FORMULATION OF VAN DER WAALS' IDEAS

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I. Introduction to the Problem

1. The Methods of Kinetic Theory

At the time when van der Waals published his famous equation of state the work was considered to be an important success in kinetic theory, whereas nowadays his line of argument is regarded as unsatisfactory. The reason for this change of attitude is a change in the aims of kinetic theory.

Towards the end of last century the theory was aiming mainly at ascertaining the properties of molecules, which at that time were considered hypothetical. We now frequently have more knowledge of the molecules than of the relation of their properties to the more complex thermodynamical phenomena.

From van der Waals' theory conclusions on molecular forces were drawn. It appeared that there was attraction and that the molecules could not penetrate each other, or, as we say now, repel each other at short distances. These inferences are not affected by the crudeness of the assumptions underlying van der Waals' theory.

Forces between molecules are now well understood and can in principle be derived from the dynamics of the electrons in the field of the nuclei. The attractive forces are, moreover, readily derived from optical data, and the molecular radius can for instance, be obtained from the properties of the crystalline phase independently of the equation of state. Monatomic molecules interact by means of relatively simple central forces.

In addition to a fair knowledge of molecular interaction, we know how the properties of matter in bulk are to be derived from the molecular model. If the potential energy of the whole system (gas, liquid) is given as a function of the co-ordinates of the molecules—this is the adequate specification of a molecular model—all that is required to obtain the thermodynamical properties is the evaluation of a certain integral.

Kinetic theory has, however, not made large contributions to the explanation of complex thermodynamical properties of matter.

There is so far no fully adequate theory of the liquid state, of phase transitions, of λ-points or of anomalous dielectric constants of crystals, etc. Mathematical difficulties are the reason for this lack of progress.

Since thermodynamical data are determined by the molecular model, a theoretical treatment must be careful not to overdetermine them by means of an additional hypothesis. Even a plausible assumption, giving results that are in agreement with observation, should be used with caution in order not to introduce an over-determination. If additional assumptions are introduced under the label of a method of approximation, they can add more to confusing the problem than to solving it. Arguments such as those used by van der Waals are, therefore, no longer accepted. Progress can be achieved only by overcoming the mathematical obstacles.

Theoretical work, in which the molecular model is evaluated without introducing additional assumptions, will at least provide new methods and is of interest from this point of view. In this article an account is given of recent theoretical work on condensation in which progress has been achieved.

2. Premisses

It is assumed that the gas or liquid consists of monatomic molecules. Every pair of molecules has an energy of interaction φ which depends upon the distance between the molecules. The interaction of one pair is not influenced by the presence of another molecule, so that the sum of the interaction of the pair-energies adds up to the total potential energy Φ

$$\Phi = \sum_{j=2}^{N} \sum_{i=1}^{j-1} \varphi_{ij}$$

where N is the number of molecules.

In this equation suffixes are used for distinguishing between the individual molecules, which are in this way "labelled."

The interaction energy φ is large and positive at small distances between the molecules (repulsion), it is small and negative at larger distances (attraction), and vanishes at distances that are small in comparison with the dimensions of the container. The molecular model is not specified in greater detail. Direct interaction of molecules is restricted to small distances. This does not exclude an indirect influence over appreciable distances when a large number of molecules is closely packed.

The energy of the gas or liquid is equal to the sum of kinetic and potential energies. Denoting the mass of the molecules by m, the

Cartesian co-ordinates of the molecules by x_i, y_i, z_i, the corresponding components of velocity by u_i, v_i, w_i, the energy is expressed as a function of these 6N variables

$$E = (m/2)\sum_{i=1}^{N}(u_i^2 + v_i^2 + w_i^2) + \sum_{j=2}^{N}\sum_{i=1}^{j-1}\varphi_{ij}$$

Every physical quantity appropriate to matter in bulk is the mean value of a quantity appropriate to the molecular model. The "mean value" is meant to be the time average over the orbits of the molecules, but is evaluated by means of the probability distribution of the instantaneous states of motion of the whole model. The instantaneous state of motion is specified by the values of the co-ordinates and velocity-components of all molecules. The probability distribution is accordingly a function of the 6N variables

$$x_1, y_1, z_1 \ . \ . \ . \ x_N, y_N, z_N, \ u_1, v_1, w_1 \ . \ . \ . \ u_N, v_N, w_N.$$

For thermal equilibrium the probability distribution is proportional to

$$\exp(-E/kT)$$

where $k = 1{\cdot}37.10^{-16}$ is Boltzmann's constant. The factor of proportionality is chosen so as to make the probability for the model having *any* state of motion equal to one. The above exponential function is accordingly divided by

$$Z = \int . \ . \ . \int \exp(-E/kT)dx_1 dy_1 dz_1 \ . \ . \ . \ du_N dv_N dw_N$$

where integration over the components of velocity has the limits $-\infty$ and ∞, and the integration over the co-ordinates is carried over all values in the interior of the container. Z is called the partition function. It no longer depends upon the co-ordinates and velocity components of the molecules, but upon the temperature and the volume.

The calculation of mean values is greatly simplified if the partition function is known, since the latter is related to the free energy according to

$$F = -kT \log Z$$

and the properties of matter in thermal equilibrium can be derived from the free energy by means of thermodynamical formulæ.

In calculating Z, the integral over the components of velocity is readily carried out and gives

$$(2\pi kT/m)^{3N/2}$$

independently of whether the molecules form a liquid or an ideal

gas. This factor of the partition function is not, therefore, of much importance in what follows.

The specific properties of a dense gas or liquid are obtained by evaluating the remaining integral over the co-ordinates; this is denoted by Q and said to be the "configurational partition function":

$$(1)\ Q = \int \ldots \int e^{-\Phi/kT} d\tau_1 . d\tau_2 \ldots d\tau_N \qquad d\tau_i = dx_i dy_i dz_i$$

The evaluation of this integral is difficult, owing to the simultaneous interaction of many molecules, which prevents the integrand from being separable into factors depending upon a small number of variables.

The equation of state as given by van der Waals is not based upon an attempt at evaluating the partition function, but upon plausible relations between the mean forces and the density, which are introduced as a hypothesis. His assumptions can be justified for low densities and high temperatures, but not for the range of condensation.

The V-P curves at constant temperature are well known. They consist of a section applying to the liquid, a section applying to the vapour, and in between a section which has no relation to physical facts. No distinction is made between saturated and supersaturated vapour, or between liquid in equilibrium and superheated liquid. The range of volumes in which part of the substance is condensed is, in fact, not covered by the equation of state. It is obtained by supplementing the equation of state by thermodynamics.

The theory is in reasonable agreement with experimental data. It provides the critical phenomena but, owing to the crudeness of the underlying assumptions, it gives no information on the specific reasons for the phenomenon of condensation.

Before turning to the modern theories, two points should be made clear.

A discontinuity of enthalpy, or any discontinuity of thermodynamic functions, cannot occur in any system of a finite number of molecules. If we speak of a discontinuity it refers to the limit of an infinite number of molecules, so that, for example, the specific heat curve has a maximum which tends to become infinitely sharp and infinite with an increasing number of molecules. It might, alternatively, tend to reach a high but finite limit. As far as boiling is concerned, the existence of a sharp transition seems to be taken for granted by all authors; there is so far no sufficient basis for investigating the other alternative.

Any theory which, like the theory of van der Waals, gives an equation of state for the liquid and vapour, but not for the 2-phase range, is in a way incomplete. If only a liquid and a vapour state are provided and no 2-phase range, this does not suggest partial condensation, but rather an oscillation of the whole system between the two states of aggregation.

II. The Theory of Molecular Clusters

3. Principle of the Method

A theory of dense gases and condensation has been given by J. E. Mayer, and supplemented by several other authors * in which an attempt is made to obtain correct relations with which the partition function (1) has to comply, *e.g.*, relations which are not sufficient for actual evaluation of the partition function ; no integrations are actually carried out. The partition function is shown to depend upon the volume at constant temperature in a way which can be foreseen independently of the possible result of integrations.

At medium densities the partition function can be expanded in a series of terms, each of which corresponds to the contribution of independent clusters of molecules. There may be many molecules in a cluster ; as long as its volume is small in comparison to macroscopic dimensions, it will not interfere appreciably with other clusters, and is not appreciably affected by the walls of the container.

The probability with which the molecules in a cluster occupy their relative positions may be a complicated function of their coordinates, but does not depend upon the volume. The contribution of the cluster to the partition function, depends in a simple way upon the volume, although it is an involved integral and neither its absolute value nor its dependence on temperature are easily accessible.

It may be said that a dense gas behaves like an ideal gas in which one molecule takes the place of one cluster. The pressure depends upon the number of clusters, but not upon their size.

The theory proceeds to express the partition function in terms of the volume and the unknown contributions of the clusters, which are called " cluster integrals."

4. Expansion of the Partition Function

According to these assumptions, the integrand of the expression

* The theory and some applications are published in references 1–10. A summary is given in *Statistical Mechanics* by J. E. Mayer and M. Goeppert Mayer, New York, 1940.

(1) is a product of terms, each of which depends upon the distance of 2 molecules:

$$\exp(-\Phi/kT) = \Pi\exp(-\varphi_{ij}/kT)$$

where Π means product, the product being taken over those pairs of suffixes for which $N \geqslant j > i \geqslant 1$. This is conveniently transformed into another product by introducing the functions

$$f_{ij} = \exp(-\varphi_{ij}/kT) - 1$$

so that the integrand is

$$\Pi(1 + f_{ij})$$

The functions f_{ij} are distinct from zero only for those small distances of the molecules i and j at which there is an appreciable interaction. The integral of f_{ij} over the co-ordinates of one molecule defines roughly the volume of the sphere of interaction. It is independent of the co-ordinates of the second molecule. Integration over the latter gives a factor V.

In the following the notion of "cluster integrals" is used, of which the integral of f_{ij} is the simplest example. The expansion of the above product gives a sum of products of functions f_{ij}. After integration a large number of terms will be equal to each other. In order to specify the terms which give the same integral it is convenient to discuss an example, *e.g.* the products of 4 factors f_{ij}. If it is $f_{12}f_{34}f_{56}f_{78}$ it refers to 4 isolated clusters of 2 molecules The product $f_{12}f_{23}f_{13}f_{45}$ refers to one cluster of 3 and one of 2 molecules. The products $f_{12}f_{23}f_{34}f_{14}$ and $f_{12}f_{13}f_{14}f_{15}$ are contributions of a cluster of 4 and 5 molecules respectively; they are of course not the only contributions of these clusters.

On integration the results differ according to the type of clusters which contribute to the integrand but are independent of the labels of the molecules. In every product the contributions of different clusters are integrated independently of each other, and integration of a product contributed by one cluster gives a quantity that is independent of the volume multiplied into V, similar to the integral of f_{ij}.

By collecting all terms originating from the clusters of s molecules, the "cluster integrals" are defined as

$$b_s = (1/Vs!)\int\ldots\int\Sigma\Pi f_{ij}d\tau_1\ldots d\tau_s$$

so that they are independent of the volume. The suffixes must satisfy the condition $s \geqslant j > i \geqslant l$ and every function f_{ij} has at least one suffix in common with one other function in the product. The sum is taken over all products that comply with these conditions.

The clusters are analysed once more. In the product $f_{12}f_{13}f_{14}f_{15}$, for instance, the integrations over 3 intermolecular distances are independent of each other, so that the integral over the co-ordinates of 5 molecules is reduced to integrations over pairs. No reduction of a similar kind is possible in integrating the product $f_{12}f_{23}f_{34}f_{14}$, where the suffixes form a cycle. An integral which cannot be split up into independent factors is called an "irreducible integral." The definition is given

$$\beta_r = (1/r!\,\mathrm{V})\int\ldots\int\Sigma\Pi f_{ij}d\tau_1\ \ldots\ d\tau_{r+1}$$

where $1+r \geqslant j > i \geqslant 1$ and where every pair of suffixes belongs at least to one cycle. The sum is taken over all products that comply with these conditions.

By means of some combinatorial arguments the partition function is expressed in terms of cluster integrals.

$$(2)\ \mathrm{Q} = \mathrm{N}!\sum_{m_1}\sum_{m_2}\ldots\sum_{m_s}\ldots\prod_{s}(\mathrm{V}b_s)^{m_s}/m_s!$$

The numbers m_s are equal to the numbers of clusters of s molecules which are present simultaneously in one configuration of the whole gas. These numbers are subject to the condition

$$(3)\ \sum_s sm_s = \mathrm{N}$$

The cluster integrals are expressed by a similar formula in terms of the irreducible integrals

$$(4)\ b_s = (1/s^2)\sum_{n_1}\sum_{n_2}\ldots\sum_{n_r}\ldots\prod_{r}(r\beta_r)^{n_r}/n_r!$$

where the numbers n_r are subject to the condition

$$(5)\ \sum_r rn_r = s - 1$$

In addition to these exact but uninformative relations it may be assumed at least that at sufficiently low temperatures the quantities b_s and β_r are positive.

Equations (2)–(5) imply a relation between the partition function and the free energy and the volume. In order to recognise its significance some transformations are necessary. For a rigorous treatment rather involved methods have to be applied. The same result is obtained in a more elementary way by replacing the right hand side of equation (2) by the largest term of the sum.

The log of a term in (2) is

$$m_s(\log \mathrm{N}vb_s - \log m_s + 1)$$

(where $v = V/N$) has accordingly to be made a maximum with equation (3) as restriction on the possible values of the m_s, so that

$$(6) \quad -\log Nvb_s - \log m_s + s \log Y = 0$$

where Y is determined by equation (3). In the largest term

$$m_s = Nvb_sY^s$$

The log of the partition function is accordingly

$$\log Q = N(\Sigma vb_sY^s - \log Y) + \log N!$$

Determination of Y requires solution of the equation

$$(3a) \quad \sum_{s=1}^{N} vsb_sY^s = 1$$

and it is the lowest positive root that is needed.

In a similar way the sum in equation (4) is replaced by its largest term. An equation similar to (6) is obtained in which an undetermined multiplier $\log \rho$ appears, which can be determined by the equation

$$(5a) \quad \sum_{r=1}^{s-1} r\beta_r\rho^r = 1$$

The quantities Y and ρ may be assumed to tend towards a definite limit independently of the number of terms in the sums of equations (3a) and (5a).

In the case of an ideal gas $Y = 1/v \ll 1$. Equation (3a) can be solved in terms of the irreducible integrals; Y is then obtained as an expansion in powers of $1/v$:

$$Y = (1/v)\exp(-\Sigma\beta_rv^{-r})$$

and
$$\Sigma vb_sY^s = 1 - \Sigma(r/1+r)\beta_rv^{-r}$$

5. Conclusions

The relevant terms of the free energy F are related to Q according to $F = -kT\log Q$. The expression for Y in terms of v can be accordingly used in order to obtain thermodynamical quantities in terms of the volume:

$$(7) \quad PV/RT = [1 - \Sigma(r/1+r)\beta_rv^{-r}]$$

$$(8) \quad V(\partial P/\partial V) = (kT/v)[1 - \Sigma r\beta_rv^{-r}]$$

Equation (7) shows that the irreducible integrals determine the virial coefficients.

Although the β_r are not known numerically, the mere fact that they do not tend to zero at high values of r (at least at low temperatures) indicates that at some characteristic value of v the virial

expansion and the other expansions occurring in the thermodynamical formulæ will no longer be convergent. The main object of the theory is the determination of the value of v at which this occurs and of the functions that are represented by the series, at values of v beyond the singularity. The mathematical argument, however, is indirect and is, therefore, not fully conclusive. In addition, the independence of the b_s of the volume is dubious in the range under consideration. Nevertheless, the result is striking in spite of possible objections.

From equation (5a) and (8) it follows that for $v = 1/\rho$, that is for a finite value of v, $\partial P/\partial V$ becomes zero. Moreover, it can be shown that for high values of s, b_s becomes almost proportional to the s^{th} power of a constant, and that for this reason the series in (3a) is divergent for a characteristic value of Y, which corresponds to the value of Y at $v = 1/\rho$. At smaller volumes Y is independent of the volume over a finite range of volumes. It follows from the relation of Y to the free energy that there is a range of volumes in which the pressure is independent of the volume.

These relations suggest that at the characteristic volume condensation occurs. This is indicated simultaneously by the divergence of the virial expansion and by the independence of the pressure of the volume.

If this interpretation is accepted, it is not difficult to recognize in the formulæ some details of the phenomena associated with condensation. If it is assumed—the assumption being plausible—that the irreducible integrals tend to become negative at higher temperatures, the existence of a critical point can be demonstrated. According to this theory there is below the critical temperature another characteristic temperature; condensation is possible only below the lower characteristic temperature; in the range between the two characteristic temperatures the pressure continuously approaches independence of volume.

According to this theory there is a range of condensation, as actually observed, and not only the liquid and vapour state as in van der Waals' equation.

It is not yet possible to say whether the above interpretation can be maintained. The lack of knowledge of the irreversible integrals is a serious obstacle for any discussion or test in terms of numerical data.

The fact that the arguments are, if not right, nevertheless possibly right, shows in any case that a consistent and rigorous theory is within reach.

III. Theory of the Average Field of Force

6. Representative Single Molecules

Since the virial expansion does not converge in the liquid state, a different approach to the kinetic theory of liquids is needed. It has been found that the assumption of one or a small number of molecules moving in an average field of force originating from other molecules is a useful approximation. In liquids there are no simple limiting laws such as the ideal gas or crystal. Nevertheless, the kinetic theory ought not to involve too great difficulties, since we know that the distribution of molecules in space is not very distinct from a random distribution, at least in so far as there is no long-distance correlation as there is in crystals. The assumption of an average field is well adapted to these conditions. There is, however, *a priori* no indication of how this average field can be introduced with a minimum of arbitrary assumptions.

In a rather crude but successful way a theory of the average field was established by Lennard Jones and Devonshire [11]. They assume that one molecule, which is regarded as representative, is enclosed in a cell, where it may move under the influence of the forces originating from the neighbouring molecules. This picture seems to be quite plausible in the liquid state. It is, in addition, shown by the authors to be valid even in the case of a dilute gas. The fact that a molecule is in reality not confined to a cell is accounted for by admitting interchanges of the molecules between different cells, an assumption that does not affect the result.

In laying down the rules according to which the average field of force in the cell is to be derived, the authors make some arbitrary assumptions. This can, however, hardly be avoided. It is assumed that the surrounding molecules are distributed uniformly over the surface of the cell. The remaining part of the theory is free from arbitrary assumptions. The potential energy is derived from the interaction of pairs, which in their turn are arrived at by methods independent of the critical data. The model is evaluated correctly and thermodynamical data are obtained.

The V-P curves at constant temperature are of the same type as those of van der Waals' equation. In addition, the absolute values of the critical data result in reasonable agreement with experiment.

This success is, of course, no justification for the crude assumptions that are introduced. The theory seems to be a good starting point for the theory of liquids, but, in the form in which it is presented, it is hardly capable of refinement.

The use of an average field has subsequently been worked by other authors into a systematic theory.

7. Distribution of Small Representative Groups of Molecules

The most detailed specification of the instantaneous state of motion of a monatomic gas or liquid consists in assigning to every molecule numerical values for its 3 co-ordinates and 3 components of velocity,* that is by means of 6N data. In Gibbs' *Statistical Mechanics* the thermodynamic properties of the system are correspondingly derived from a probability distribution in these 6N variables, as explained in section II.

In the kinetic theory of gases distributions in 6 variables are frequently used, *e.g.* the co-ordinates and components of velocity of one representative molecule. In the theory of Brownian movement, distributions in 3 co-ordinates only are sometimes employed.

A distribution of one particle gives less information than a distribution of the whole system. It is, however, easier to handle and has proved to be sufficient for the kinetic theory of dilute gases and suspensions. In the theory of Lennard Jones and Devonshire an application of such a distribution to the theory of liquids is made which is obviously not wholly satisfactory.

It may be added that the changes in time of the different types of distributions are governed by different dynamical laws. For the distribution of the whole system Gibbs has given the dynamical equation; † for dilute gases the integro-differential equation of Boltzmann, which is based on the probability of collisions, applies, and for the distributions of Brownian particles the change in time is given by Smoluchowski's equation.

Generalising these ideas, distributions for representative pairs of molecules, or representative groups of 3, 4, . . . *r* molecules are defined. They provide more information than the distribution of one representative molecule and are easier to handle than the distribution of the whole system. They are likely to be of great use in the kinetic theory of liquids. They may refer to the distribution in co-ordinates and velocities or co-ordinates only.

A distribution of representative pairs of molecules in a liquid has been in fact recognized to be the appropriate way of interpreting X-ray interference patterns. The importance of these distributions for the theory of transport processes in liquids has been recently

* In statistical mechanics it is usual to speak of momenta rather than of velocities. In the case of monatomic systems this does not make an essential difference.

† This equation is also known as Liouville's theorem.

recognised by Kirkwood [13], who derives their dynamical equations from the principles of statistical mechanics and has in this way provided the basis for the interpretation of diffusion, viscosity and thermal conductivity of liquids. Born and Green * have made a systematic study of distributions of this kind and have obtained results concerning condensation.

There are some obvious relations between the different kinds of distributions on which the further argument is founded.

From a distribution of r molecules the distribution of a smaller number of molecules s, is obtained by taking an average over the variables appropriate to r minus s molecules.

From a distribution in co-ordinates and velocities the distribution in co-ordinates only is obtained by taking an average over the velocities.

While it is possible to define distributions in co-ordinates, velocities and accelerations, the latter can be eliminated by means of their relation to the force which, being derived from a potential, is a function of co-ordinates.

The dynamical equations are derived by a straight argument from first principles. Consider at first a distribution in co-ordinates. Its change in time within one volume element involves a flow to neighbouring volume elements in order to comply with the conservation of matter. Since the flow is proportional to velocity, it can be derived by an averaging operation from the distribution in co-ordinates and velocities. The time derivative of a distribution in co-ordinates accordingly depends upon an integral over the distribution in co-ordinates and velocities.

Similar arguments apply to the change in time of a distribution of r molecules in co-ordinates and velocities. This depends upon an average acceleration, which in its turn is expressed in terms of an integral over the distribution of $r + 1$ molecules.

From the general dynamical equation for distribution Born and Green obtain a relation which holds for thermal equilibrium :

$$(9) \quad \frac{\partial \rho^{(r)}}{\partial x_i} + \sum_{j=1}^{r} \frac{\rho^{(r)}}{kT} \frac{\partial \varphi_{ij}}{\partial x_i} + \int \frac{\rho^{(r+1)}}{kT} \frac{\partial \varphi_{i(r+1)}}{\partial x_i} d\tau_{r+1} = 0$$

Here the suffixes refer to the labels of the molecules and $\rho^{(r)}$ is the distribution of r molecules in co-ordinates only. φ_{ij} has the same meaning as in section II. This equation is independent of the general relation expressing the distribution of a smaller group of molecules as integral over a distribution of a larger group. The

* *Cf.* references 14–16. The results of these authors for transport processes are not yet published.

meaning of equation (9) is readily recognized by considering the theory of Brownian movement. There the expression

$$\frac{\partial \rho^{(i)}}{\partial x} - \rho^{(i)}X$$

(where X is the x-component of force) multiplied into kT and divided by a friction constant is the negative x-component of the flow. In thermal equilibrium the flow is 0. Equation (9) is the corresponding statement for a distribution of r molecules specifying the origin of the force, part of which is due to molecules outside the group of r molecules.

8. The Theory of Representative Pairs

At this point Born and Green introduce an assumption which in a way plays the part of the assumptions of Lennard Jones and Devonshire. They let the distribution in the liquid depend upon the distribution of a representative pair of molecules. Equation (9) (with $r = 2$) contains a distribution of a group of 3 under the integral. This is assumed to be determined by the distribution of pairs according to

$$\rho^{(3)}_{123} = \rho^{(2)}_{12} \cdot \rho^{(2)}_{13} \cdot \rho^{(2)}_{23}$$

This is, of course, an arbitrary assumption. It is, nevertheless, a big advance on the assumptions of the cell theory. It determines automatically the field of force for the pair, whereas the determining of the field in a cell requires additional assumptions. It is, in principle at least, capable of refinement by specifying conditions in the liquid in terms of a distribution $\rho^{(3)}$ and expressing the $\rho^{(4)}$ under the integral in terms of distributions $\rho^{(3)}$.

By means of the approximation equation (9) is transformed into an equation containing only one unknown function, *i.e.* $\rho^{(2)}$, which can be determined by solving the equation. Transformation into a linear integral equation * enables the authors to give a solution in terms of a complex integral. The latter depends upon the Fourier transform of the function

$$s[\exp(-\varphi^{(5)}/kT) - 1]$$

where s is the distance between the molecules of a pair and the expression in the bracket is the function f_{ij} as employed in section II.

The solution depends upon the path of integration and the authors show that there are in general two possibilities for this path. The two solutions are identified as corresponding to the liquid and the vapour. As in van der Waals' theory there is no distinction between stable and metastable ranges.

* A similar equation was given by Kirkwood and Boggs [12.]

In addition, the authors give a method for calculating the virial coefficients which does not involve unduly great difficulties. In following up this line the particular method of approximation may possibly have some effect on the result, since it does not account for the particular kind of correlation that is specific for the simultaneous interaction of many molecules.

The relation between the two theories, of which an account is given in this article, is not yet fully established. Born and Green say that their result demonstrates the 2-phase range of the cluster theory as being spurious.

This conclusion does not seem to be a necessary consequence of the different kind of result provided by the two theories. The theories of representative single molecules or pairs seem to imply that these representative groups refer to one, possibly metastable, phase. It is accordingly reasonable that these theories give an alternative for the phase to which the molecules or pairs belong. The cluster theory refers to the whole system in stable thermal equilibrium and must be expected to give a 2-phase range.

Since the second theory applies to the liquid and gas phase, the first at the best to the gas, admitting a slight extrapolation into the 2-phase range, the second seems to be the more powerful method. It is, however, likely that a detailed specification of the condensation process will require the further development of the first method.

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RECENT ADVANCES IN SCIENCE

PHYSICS. By F. A. Vick, O.B.E., Ph.D., F.Inst.P., The University, Manchester.

Friction between Solid Bodies.—Most of us while at school or university considered the theoretical and experimental study of friction to be the dullest part of our courses, and were thankful to leave the subject for others more obviously interesting or exciting. Yet, most of us would now agree, on reflection, that the study of friction between solid bodies is of supreme practical importance, and will be surprised to learn that there is still considerable controversy as to the nature of the forces involved. The number of papers published on the subject appears to be increasing rapidly.

It will be as well to begin with definitions of terms, since some of them are used differently by different people. Following Schnurmann (*Phys. Soc. Rep. Progr. Phys.*, **8**, 74, 1941), " solid friction " is used for the tangential forces between perfectly clean dry surfaces (without adsorbed layers) ; " dry " and " ordinary " friction between the normal dry surfaces in air, when no lubricant has been added intentionally ; " boundary lubrication " covers all those cases in which the surfaces are separated by a film of lubricant too thin to be considered as a fluid.

Frictional forces have at various times been ascribed to various causes such as (1) adhesion between solid surfaces by molecular forces akin to cohesive forces ; (2) irregularities in the surfaces ; projections in the top surface fitting into hollows in the lower, and having to be lifted to slide over the projections in the lower, *i.e.* to slide up successions of small slopes ; (3) projections in the harder surface cutting through projections in the softer ; (4) electrostatic (boundary layer) forces. Many recent workers consider the frictional forces to be a combination of two or more of these. The energy dissipated in overcoming the frictional forces may be transformed to (i) heat energy (including elastic energy of deformation, changing later to heat energy) ; (ii) cold working of surfaces, *i.e.* changes in crystalline form ; (iii) increasing surface energy by tearing particles from the surfaces, including the transfer of matter from one surface to the other.

Some of the work carried out between 1500 (Leonardo da Vinci) and 1941 is summarised by Schnurmann (*loc. cit.*). The familiar empirical law first proposed by Amontons (1699) and investigated

by Coulomb (1785), $F = \mu N$ where F = tangential force, N = normal load and μ the coefficient of friction (independent of the area of contact) is useful in distinguishing between relative motion by sliding and by tearing, since the law breaks down in the latter case. By 1941 it was recognised that wide variations of μ for static "dry" friction in air are due largely to varying degrees of contamination in the form of adsorbed layers. It had been verified that surfaces nominally plane are really mazes of microscopic irregularities, so that if surfaces are in contact (no adsorbed layers) frictional forces must arise at those irregularities which carry the load. The irregularities could then suffer elastic deformation and abrasion during sliding, the former leading to appreciable temperature dependence of frictional work converted to heat and the latter practically temperature independent. A criterion between the two mechanisms would thus be a determination whether, over a wide range of temperatures down to the absolute zero, the amount of mechanical work varies with the temperature of the system. Schnurmann summarises some of the experimental determinations. Results so far are not very clear, though a small temperature coefficient is found in some cases. It was well-known by 1941 that under certain conditions the sliding motion of bodies elastically restrained does not always proceed smoothly, but sometimes in jerks, exhibiting the characteristics of relaxation oscillations, with fixed amplitude. Schnurmann's view was (see Schnurmann and Warlow-Davies, *Proc. Phys. Soc.*, **54**, 14, 1942) that this behaviour might be due to surface electrification, which occurs whenever two different materials establish contact. The separation of electrical charges occurs only at the small areas actually in contact; in those cases in which the charges have fixed positions on the surfaces (dielectrics or metal surfaces coated with dielectric films) the charges become separated as sliding proceeds. These give rise to a tangential electrostatic force which increases as new contacts are made until the dielectric breakdown strength is reached, leading to rapid discharge and a repetition of the slow charge. Schnurmann describes experiments in support of his views. Bowden and Laben, on the other hand, had earlier (*Proc. Roy. Soc.* **A.169**, 371, 1939) proposed a quite different interpretation of the "stick-slip" behaviour. They ascribed it to the properties of the sliding metals themselves, especially the welding together of the metals at local places of contact, following local melting. "Stick-slip" is, however, observed for rubber on glass, wood on metal, etc. We shall return to this question later in this article. Schnurmann goes on to mention measurements of surface temperatures during sliding, particularly applications of the ingenious method devised

by Bowden and his collaborators of using the rubbing contact of two different metals as a thermocouple. It appeared that large values of the frictional force and of the speed of sliding are necessary for achieving appreciable rise of temperature of the contact surface of a metal. For example, with gallium on steel, a speed of 720 cm. per sec. at a load of 27 gm. wt. was required to bring the surface of gallium to its melting-point (30·2° C.).

Turning now to more recent work, Bowden, Moore and Tabor (*J. Appl. Phys.* **14**, 80, 1943) describe further experiments on the adhesion and ploughing of sliding metals. As indicated above, Bowden and his colleagues consider that frictional resistance between unlubricated metals is due mainly to a combination of the shearing of metallic junctions formed by adhesion and welding at the point of contact, and of the work of dragging or ploughing the surface irregularities of the harder metal through those of the soft one. In this investigation they adopt a method of micro-examination of the metal surfaces developed by Nelson, in which the surface is first protected by depositing on it another of similar hardness, and then cutting a section at a very oblique angle to the plane of the surface. If this angle is 6°, for example, the contour of the surface has its vertical component magnified about ten times. One of the micro-photographs published shows the track formed by sliding a slightly worn hemispherical steel slider at a slow speed over a mild steel surface (unlubricated). A considerable area of the surface is seen to be unchanged, but at a number of points penetration, ploughing and tearing of the metal have occurred, while at other points the metal is raised above its former level. Another photograph is for a copper slider on unlubricated steel, in which no ploughing is seen but some fragments of the copper are left welded on to the steel. Under the copper welds, there is some evidence that the steel is deformed. (Schnurmann had already shown (*J. Appl. Phys.*, **13**, 235, 1942) that the harder of two metals shows characteristic traces of the softer metal on its surface after sliding.) In each case, the sections are cut perpendicular to the direction of sliding. The adhesion and welding has apparently occurred at comparatively low surface temperatures. In their experiments, the lower surface is driven along at a uniform rate by a water piston, and the upper slider is in an elastic support. " Stick-slip " is observed under some conditions, and Bowden, Moore and Tabor point out that the motion is influenced by the elastic and mechanical properties of the system. The authors then go on to examine quantitatively their suggestion as to the nature of the frictional forces. If frictional force $F = S + P$, where S is the force required to shear the metallic

junctions and P the force to displace the softer metal from the path of the harder, then $S = As$, where A is the actual area of contact of the metals, and s the shear strength of the soft metal. When the load is applied to the surfaces the softer metal flows plastically until A is sufficiently great to support the applied load. For a particular metal, therefore, $W = pA$ where p is the " flow pressure " necessary to cause plastic flow. Also $P = A'p$ where A′ is the cross-section of the torn track of the soft metal. Then,

$$F = \frac{Ws}{p} + A'p$$

and $$\mu = \frac{F}{W} = \frac{s}{p} + \frac{A'p}{W} = \frac{\text{Shear strength}}{\text{flow pressure}} + \frac{A'p}{W}$$

If the ploughing term is negligible

$$\mu = \frac{\text{Shear strength}}{\text{flow pressure}}$$

for the softer metal, and Amonton's law of friction holds. Bowden, Moore and Tabor describe experiments for steel sliding on indium, using sliders of simple geometric shapes, and show that the results can be interpreted approximately by an application of the theory just outlined. It might be interpolated here, that many workers prefer to reserve the term " friction " for those cases in which no " ploughing " or scratching occurs.

In a following paper (*J. Appl. Phys.*, **14**, 141, 1943) Bowden and Tabor examine the effect of thin metallic films on frictional forces. According to the theory just given, the friction on various soft metals should be approximately proportional to the shear strengths of the metals, and this is found to be so for indium, lead and copper against steel. With a thin film of indium, the coefficient of friction was found not to be independent of load, but to decrease with increasing load. The authors believe that the efficiency of some bearing alloys is due to the spreading over the surface of thin films of the soft-metal constituent of the alloys.

In an interesting review paper (*Rev. Mod. Phys.*, **16**, 53, 1944), J. J. Bikerman summarises first various methods of determining the degree of surface roughness, and then goes on to show how the Amontons (Coulomb) law of friction can be derived from the mechanism of the slider climbing the slopes of the irregularities on the lower surface. The coefficient of friction is only statistically determinable, owing to the variation in the slopes of the "hills", which are somewhat deformed by the load. The observed values

of μ lead to the average angle between hills and surface plane being within the range 6° to 26°, for, if the angle is α, the component of the pulling force f acting along the slope is $f \cos \alpha$, the component of the weight W of the slider acting down the slope is $W \sin \alpha$. When there is no acceleration, $f \cos \alpha = W \sin \alpha$ and $\mu = \tan \alpha$. Bikerman believes that adhesion (molecular cohesive forces) cannot be the explanation of ordinary dry friction, because, when the contact between two solid surfaces is so intimate that their mutual attraction cannot be neglected, they stick together and do not slide in conformity with the law of friction. According to this view, sliding takes place under dry friction conditions because the surfaces are never in intimate contact; they are always separated by gas or liquid films. If molecular adhesion is important, the force should be apparent as one operating normally to the interface, of the same order of magnitude as the frictional force. There are other objections to adhesion being the only cause of frictional forces. Bikerman appends to his paper a very useful collection of references to earlier work.

The experiments of Bowden, Moore and Tabor outlined above indicated that, even under light loads, metal may be exchanged between sliding surfaces. Radioactive tracer elements have been used by Sakmann, Burwell and Irvine (*J. Appl. Phys.*, **15**, 459, 1944) to obtain more quantitative estimates of the amounts of metals transferred. The method consists of artificially activating one of the surfaces and measuring the activity acquired by the other surface. In the experiments described, polished beryllium-copper was exposed to a deuteron beam in a cyclotron:

$$Cu^{63}_{29} + H^2_1 = Zn^{63}_{30} + 2n^1_0$$
$$Cu^{63}_{29} + H^2_1 = Cu^{64}_{29} + p^1_1$$

The Zn isotope decays with a half-period of 38 minutes and the Cu of 12·8 hours. The surface was then electro-polished to remove loose particles, and hemispherical or spherical riders of $\frac{1}{16}$ in. radius slid over it, at about 3–4 mm./sec. The riders were tested for radioactivity with Geiger-Müller counters. 10^{-4} microgram of transferred active material could be detected. In the first group of experiments, riders of very different properties were slid over the Be-Cu block under identical conditions, with the following results:

phosphor bronze rider	0·043 micrograms deposited
steel rider	0·0064 ,, ,,
glass rider	0·0053 ,, ,,

The fact that even a non-metallic substance like glass takes up a small amount of base material is interesting. Further experiments

showed that the amount of base metal adhering to the rider was proportional to the load and increased with distance of travel, and under otherwise identical conditions the amount deposited depended on the surface finish and hardness of the rider. The amount of base metal deposited on steel riders was inversely proportional to their Brinell hardness. For riders of different materials but having the same hardness and surface finish, the amount of transferred metal increased with the solid solubility of the base metal in that of the rider. Lubrication decreased the transfer.

In a paper devoted mainly to the detonation of explosives (*Proc. Roy. Soc.*, **A.188**, 329, February 1947), Bowden, Stone and Tudor demonstrate the occurrence of " hot spots " when metals or non-metals slide over each other. When one surface was of glass or quartz, the hot spots were visible and could be photographed. The loads and relative speeds necessary to produce hot spots when both slides were good conductors were, of course, greater than for slides of poor conductors, when quite moderate speeds and loads were sufficient.

In a still more recent paper (*Proc. Roy. Soc.*, **A.189**, 88, March 1947) J. R. Bristow describes careful experiments to determine the change of " Kinetic " coefficient of friction, μ_K, with relative speed. He believes that " stick-slip " is really a relaxation oscillation dependent on the dynamics of the sliding system, the speed of sliding and the nature of the dependence of μ_F on velocity. According to this view, for relaxation oscillation to occur it is sufficient that μ_F decreases with increasing velocity at low speeds. Apparatus is described for the determination of the dependence of μ_F on speed at low speeds, and results are given for (i) a series of ethyl esters of fatty acids between hard steel and hard steel or phosphor bronze and hard steel, at room temperatures ; (ii) mineral oil containing various percentages of oleic acid, between steel and steel, or brass and hard steel, at room temperatures ; (iii) for ethyl palmitate between tin and hard steel, and mineral oil between steel and steel, at various temperatures. The curves show in some cases μ_K increasing with velocity (no relaxation oscillations) and others decreasing with increasing velocity (relaxation oscillations possible).

It is not possible, of course, in such a short space to review all the work carried out on friction between solid surfaces during the last five years, but perhaps the above examples will indicate the various methods of approach and the differing points of view. It is again true to say that the apparently simple everyday phenomena are often those which turn out to be the most complicated and difficult to interpret.

METEOROLOGY. By P. A. SHEPPARD, B.Sc., F.Inst.P., Imperial College of Science and Technology, London.

THE CONSTITUTION OF CLOUDS AND THE FORMATION OF RAIN

1. THE INITIAL PROCESS OF CONDENSATION

There is now universal agreement among meteorologists that the formation of a cloud droplet is the result of condensation of water vapour on a hygroscopic nucleus. From the dependence of atmospheric visibility upon relative humidity in areas not affected by dust and smoke (H. L. Wright, *Quart. J.R. Met. Soc.*, **65**, 411, 1939; **66**, 66, 1940) it is apparent that the size of hygroscopic nuclei, which control the visibility, is independent of relative humidity when the latter is below about 70 per cent., but increases smoothly with the humidity above that limit. Simpson (*Quart. J.R. Met. Soc.*, **67**, 163, 1941) infers from this that the nuclei cannot be solid for, he says, a solid nucleus would increase or decrease in diameter quite suddenly with an infinitesimal rise or fall in relative humidity above or below that corresponding to equilibrium over a saturated solution of the material concerned, and of this there is no evidence. Thus sea-salt nuclei, which undoubtedly exist in the atmosphere, and which have been widely accepted as primarily responsible for cloudy condensation, are now held by Simpson to be inoperative in this respect, and for the further reason that sea-spray is thought to be incapable of producing nuclei of an appropriate size, about 0·1 to 1 μ diameter, in quantities sufficient to make good the loss from the atmosphere by rain. He considers, on the other hand, that the effective nuclei must be liquid, probably acid, *e.g.* nitrous acid, and in this supports Findeisen (*Met. Zeit.*, **54**, 377, 1937). But the matter is not yet by any means settled. The behaviour of a droplet solution of a mixture of salts, as is sea-salt, in an atmosphere in which there are spatial variations in relative humidity, is not likely to provide the clear-cut discontinuity in the visibility, relative humidity curve demanded by Simpson. There is also some evidence that acid nuclei, as produced for example in combustion, are very small, giving rise to large ions of diameter about 10^{-6} cm., and these require considerable supersaturation to grow into visible droplets on account of the Kelvin curvature effect. But appreciable supersaturation (with respect to water) almost certainly does not occur in the atmosphere. Evidence on the constitution of nuclei from the electron microscope would be very welcome.*

* Two recent papers by Dessens (*Ann. Geophys.*, **2**, 276, 1946; *C.R.*, Paris, **223**, 915, 1946) throw valuable light on the nature of condensation nuclei. The nuclei were caught on fine threads of gossamer and examined

Although the assumption of sea-salt as the material of condensation nuclei can no longer be accepted without further investigation, a paper by Köhler (*Nova. Acta. Reg. Scient., Upsala*, Ser. 14, **12**, No. 6, 1941) on the range of diameters of droplets produced by a jet of air impinging on sea water is of interest. Using a Millikan chamber, he found spray droplets with diameters less than 0·3 μ — the lower limit of measurement—with a majority of drop diameters between 0·3 μ and 0·7 μ, the contained sea-salt varying between 2×10^{-14} gm. and 10^{-13} gm. per drop. These observations appear to dispose of the occasional criticism that spray droplets and the resulting nuclei are not produced with sufficient smallness to remain air-borne indefinitely.

Although the nature and properties of hygroscopic nuclei responsible for the formation of water droplets in the atmosphere (at temperatures below as well as above 0° C.) is still in some doubt, the position regarding the nature and numbers of ice sublimation nuclei is even less satisfactory. Evidence has, however, been produced from high-flying aircraft equipped with a frost-point hygrometer (Dobson and Brewer, *J.R. Aero. Soc.*, **50**, 1946) that the atmosphere at levels where the temperature is below about − 10° C. is frequently supersaturated with respect to ice, though still unsaturated with respect to water. The inference is that sublimation nuclei are either frequently absent from the middle and upper levels of the troposphere, or else are so small (10^{-6} cm. in diameter or less) as to require considerable supersaturation to become effective. (The common occurrence of persistent condensation trails produced by high-flying aircraft in a mainly clear sky is to be accounted for by the aircraft exhaust providing the necessary

under the microscope, and were found to consist of a few relatively large droplets or particles, 1 μ to 10 μ in radius, a much greater number of smaller droplets or particles from 0·3 μ to 0·5 μ in radius, and a few too small to measure. The first two groups of nuclei tend to remain liquid at humidities far below the equilibrium value for a saturated solution, *i.e.* they then largely consist of droplets of supersaturated solution. But crystallisation occurs sooner or later—the more readily the larger the droplet and the lower the relative humidity—and the almost instantaneous evaporation which then takes place often leads to a sort of explosion in which several very small crystals may be produced, later to exist for most of their lives in liquid form. To the production of several small crystal nuclei from one larger nucleus at low humidities Dessens attributes the higher observed concentration of nuclei over land, where the humidity is not unlikely to be low, than over the sea.

The crystals are sometimes cubic and likely then to be sodium chloride, but more often they are not cubic and are possibly then salts of magnesium or ammonium. (Added in proof.)

nuclei of sublimation in a supersaturated atmosphere.) Further, the fact that ice crystals are rarely, if ever, formed in a rising current of saturated air at temperatures above about $-10°$ C. suggests that the sublimation nuclei are *always* so small as to require appreciable supersaturation—saturation with respect to water at $-10°$ C. produces a relative humidity of 110 per cent. with respect to ice (see Simpson, *Quart. J.R. Met. Soc.*, **67**, 99, 1941). The existence of such fine solid nuclei (for sublimation nuclei are presumably necessarily solid) is itself a problem, for hitherto it has been supposed impossible to produce solid particles less than 10^{-5} cm. in diameter by disintegration of larger masses.

Pure ice crystal (Cirrus) clouds are, of course, quite common, but they are notable for the rather large size and smallness in number (1 to 10^{-2} cm.$^{-3}$) of the constituent crystals (Findeisen, *Microphysics of Clouds,* International Aerological Commission, Berlin, 1939). Thus, the number of *effective* sublimation nuclei is small, a point of interest in relation to the fact mentioned above that on many occasions no cloud is formed in considerably supersaturated air. Regarding this point, Findeisen (*Met. Z.*, **59**, 349, 1942) claims evidence for a "spectrum" of sublimation nuclei, and he finds further that two markedly different types occur, one effective mainly in the range between $-10°$ C. and $-20°$ C. with concentrations varying between one and a few hundred per litre, the second effective between about $-25°$ C. and $-35°$ C. with concentrations often exceeding 1000 per litre.

The problem of ice crystal formation has been studied intensively in Germany immediately before and during the war, and a certain amount of order has been brought into the subject, mainly on lines developed from Volmer's germ-theory. There is no space here to go into detail, for which the reader is referred to Krastanov (*Met. Z.*, **57**, 357, 1940; **58**, 37, 1941; **60**, 15, 1943; **61**, 19, 1944), Wall (*Met. Z.*, **59**, 177, 1942; **60**, 94, 1943), Schwertfeger (*Met. Z.*, **60**, 191, 1943) and Findeisen (*loc. cit.*, 1942).

Cwilong (*Nature*, **155**, 361, 1945) has made carefully controlled experiments with a modified Wilson cloud chamber on the nature of condensation products as a function of temperature below 0° C. He finds that in air thoroughly cleaned by repeated expansion liquid water droplets only are formed down to $-35°$ C. $\pm 0{\cdot}1°$ however big the expansion ratio. As the expansion temperature falls below $-35°$ C. ice crystals appear with water droplets, the proportion of ice crystals increasing with lowered temperature, and water droplets cease to appear at about $-50°$ C. The appearance of the solid phase does not depend on the supersaturation. Below $-80°$ C.

the number of particles formed decreases and a few appear as relatively large grains of soft hail, while below − 120° C. no particles are formed. The density of the ice cloud is increased by X-ray ionisation, but the limiting temperatures are unchanged.

In ordinary atmospheric air the limiting temperature of − 35° C. increases to − 27° C. ± 0·5°, and with the admission of tobacco smoke to − 23° C. The other changes noted above are the same as in pure air. Cwilong does not state the supersaturations attained, but he remarks that ice crystals are formed at supersaturations far smaller than those necessary to form water droplets.

2. The Sizes of Cloud Droplets and the Water Content of Clouds

A good deal of effort has been directed in recent years to the determination of the mean size and distribution of diameters (up to about 100 μ, the rather arbitrary limit between cloud and drizzle drops) of the droplets composing clouds, the importance of such data being in respect of the mechanism of cloud growth and also in relation to a number of practical problems such as aircraft icing and radar echoes from clouds. Two main lines of approach have been developed. The first, a direct method, consists in the capture of cloud droplets on a suitably prepared and exposed surface, and the later counting under the microscope of the droplets or their impressions with reference to the diameters. The recent exponents of this method are Houghton and Radford in the United States (*Mass. Inst. Techn.*, *Pap. Phys. Ocean. and Met.*, **6**, No. 4, 1938) and Bricard at the Puy de Dôme in France (*La Mét.*, **15**, 83, 1939 ; *C.R. Acad. Sc., Paris*, **214**, 439, 1942 ; see also Pauthenier and Brun, *ibid.*, **211**, 295, 1940, and Coulomb and Loisel *La Physique des Nuages*, Paris, 1940). A second, indirect method, used largely in relation to the investigation of ice accretion on aircraft flying through clouds of supercooled water drops, consists in observing the nature and the amount of rime deposited on cylinders of varying diameter exposed to the windborne cloud elements. This method has been used by Diem, simultaneously with the first method described above, on aircraft in Germany (*Ann. Hydr. u. Mar. Met.*, **70**, 142, 1942), and on aircraft in the United States and at the Harvard meteorological observatory on Mount Washington (Dolozel, Cunningham and Katz, *Bull. Amer. Met. Soc.*, **27**, 261, 1946) ; it gives in the main a kind of average drop diameter. The estimation of drop diameter from the angular radius of coronæ produced by clouds has also been used, but the method is poor ; there is generally little precision to the measure-

ment, on account of the vagueness of the coronæ—evidence of a dispersion in drop diameter—and the order of the corona observed is sometimes doubtful.

Houghton and Radford used glass slides coated with vaseline and ovened at 150° C. to provide a uniform surface. The slide was exposed to fog or cloud for an unmeasured time sufficient to ensure an adequate sample, the deposit was photographed and the drop diameter distribution determined. Here accuracy depends on (*a*) obtaining a true sample from the cloud or fog; (*b*) preventing evaporation (or condensation) between sampling and counting ; (*c*) establishing the appropriate law of flattening of the drops in the collecting medium ; (*d*) avoiding impact shattering and coalescence of the precipitated drops. A very thorough experimental and theoretical investigation of these matters by Langmuir (*General Electric Report*, "Supercooled Water Droplets in Rising Currents of Cold Saturated Air", Parts I and II, 1944 ; see also Dolozel *et al.*, *loc. cit.*), shows that appreciable errors may arise on all the above counts and that it is in fact exceedingly difficult to obtain accurate size-distribution curves and mean particle diameters by this method. He suggests, for example, that Houghton's figures for mean diameter may well be 35 per cent. too high in certain cases, with corresponding errors in mass distribution. Langmuir does, however, show that the method is capable of giving accurate values for particles down to 5 μ in radius, provided a number of conditions are rather exactly fulfilled, the most important being that the covering fraction (the fraction of surface covered by drops) should be almost exactly 0·1. In the course of these tests Langmuir showed that a hydrophobic surface dusted with soot was much better than Houghton and Radford's vaseline-coated slides. The drops make a permanent impression on the soot and the behaviour of drops after impact is then of no consequence to the later measurements. Langmuir speaks of using this technique in clouds, but so far no representative results appear to have been published. A well-developed instrument which makes use of the impression technique, on magnesium oxide rather than soot (other suitably prepared slides may also be used), has been described by Mays (*J. Sci. Instr.*, **22**, 187 and 247, 1945) and has been termed the Cascade Impactor. It embraces a series of four jets and slides, so designed that an automatic grading of the particles is provided, counting is facilitated and a check provided against coalescence or evaporation of droplets on the last three slides when coated in oil. The instrument is capable of dealing accurately with particles from 1 μ to 50 μ diameter, and valuable information may be obtained for particles up to 200 μ. It has been

used on aircraft flying in cloud in this country, but so far no systematic observations have been published.

Bricard's earlier measurements were made using a technique similar to Houghton and Radford's, but he, and Pauthenier and Brun (*loc. cit*), have also used electrostatic precipitation in a cylindrical condenser, the wall of which is covered with paper impregnated with methylene blue. Each drop leaves a permanent stain of a size related to the drop diameter, the relation to be determined by a rather difficult calibration.

In view of Langmuir's findings mentioned above, it is doubtful whether any great precision can be attached to the measurements of drop-size distribution so far published, and in any case such measurements have largely lacked the coherence necessary to enable them to be systematised in relation to the other relevant meteorological variables. The whole experimental problem is, indeed, extremely complex and requires very great effort, particularly if all necessary observations are to be obtained in the range of representative meteorological conditions. Certain important results have, however, been arrived at and are probably acceptable, except as to the absolute values which have been quoted. Thus droplet diameters at any one position in a cloud at a given instant cover a considerable range, but there is always a fairly well-marked maximum in the drop-diameter spectrum and in the volume-distribution curve, *i.e.* in the curve of nd^3 against d, where n is the number of drops of diameter d. The position of the maximum varies from one part of a cloud to another, and is mainly different in different types of cloud. Thus Houghton and Radford, *working in sea fog*, found maxima in forty volume distribution curves ranging from 12 μ to 90 μ, but with a marked predominance between 40 μ and 50 μ (Langmuir's analysis suggests these values may be high), with about 30 per cent. of the total liquid water content contained in a 10 μ band centred on the individual maxima. The distribution curve was found to remain practically the same in a given fog over a period of several hours. The mean drop diameter in most *clouds* is certainly much less than in sea fog. Thus Bricard gives mean values for the mean drop diameter of 10 μ in nimbostratus, 8 μ in stratocumulus, 6 μ in cumulus and 4 μ in stratus (cumulonimbus clouds, it is to be noted, are not included), while Diem's values are appreciably larger, but still much below Houghton and Radford's for fog. The number of drops per unit volume of cloud is of the order of a few hundred per cm.^{3}, largely independent, as far as can be seen from integrated dispersion curves, of the liquid water content of the cloud, while increase of the latter is associated with some increase in mean drop

diameter and of the maximum in the volume distribution curve in a given type of cloud. (See also below.)

The indirect method of investigating cloud structure by the deposition of rime on fixed or rotating cylinders has added very considerably to our knowledge for clouds composed of super-cooled drops, thanks largely to the work of Langmuir (*loc. cit.*). The technique developed arises from the fact that the droplets in a stream of air approaching a circular cylinder, held with axis normal to the wind, are deflected from their original paths by an amount depending on the diameter of the droplets and the cylinder and on the wind speed. The catch of the cylinder increases with increase in drop diameter and wind speed and with decrease in cylinder diameter, according to a theoretical treatment suggested by Taylor (*Rep. and Mem., Aero. Res. Com.*, No. 2024, 1940) and developed by Glauert (*ibid.*, No. 2025, 1940). If the cylinder is fixed the deposition of rime is asymmetric about the cylinder axis, building out from the forward stagnation point, and the theoretical treatment quickly loses validity, but if the cylinder is rotated the catch is symmetrically deposited and the theoretical treatment retains validity. Glauert's treatment is based on the applicability of Stokes' Law for the particles composing the cloud, whereas at high wind speeds or at aircraft speeds this ceases to be adequate for drops more than a few microns in diameter. Langmuir has therefore extended Glauert's treatment to take account of the departure from Stokes' Law, using the differential analyser for the solution of the equations of motion in this case. If now a number of rotating cylinders of varying diameter are mounted side by side, the differing catch per unit width of the respective cylinders enables the total water content of the cloud and the diameter of the droplets to be deduced (the procedure amounts in effect to extrapolating to zero diameter of cylinder). In fact, the Glauert theory is valid for one size of drop only, but Langmuir has shown that the diameter of the drops deduced from the measurements of deposition is equal to the volume-median diameter, *i.e.* a diameter such that half the liquid water content is in droplets of larger diameter and half in droplets of smaller diameter, provided the volume-distribution curve is not materially broader than observed by Houghton and Radford (*loc. cit.*). If the dispersion is materially larger than this the calculated diameter is a few per cent. greater than the volume-median diameter, but there is then usually evidence from the deposition on the larger cylinders that the dispersion is anomalous.

Langmuir has analysed riming data obtained on Mount Washington, elevation 6290 ft., in wind speeds ranging from 24 to 110 mi./hr.,

in temperatures from $-25°$ F. ($-32°$ C.) to $+29°$ F. ($-2°$ C.), and in clouds whose liquid water content varied from 0·091 g.m.$^{-3}$ to 1·13 g.m.$^{-3}$, volume-median drop diameters from 6·4 μ to 24 μ and drop concentrations from 47 cm.$^{-3}$ to 1560 cm.$^{-3}$. He found that the volume-median drop diameter d_{vm} (in μ) is related with air temperature T (° F.), water content w (g.m.$^{-3}$), and wind speed V (mi./hr.) by

$$d_{vm} = 0{\cdot}015(74 + \mathrm{T})\left(\frac{1000w}{\mathrm{V}}\right)^{0{\cdot}40}$$

the agreement of the experimental data with this formula being very close in respect of w/V, a source of large variation in d_{vm}, but rather poor in respect of T, a source however of much smaller variation in d_{vm}. The increase of d_{vm} with T and w is rightly regarded by Langmuir as an important meteorological result which he goes on to relate with the process of drop growth (see para. 3 below). The dependence on wind speed is, however, not to be regarded primarily as a meteorological phenomenon but arises from the particular site of observation ; the wind speed is, in fact, a measure of the vertical velocity of the air in the cloud moving up the slope of the mountain and is, therefore, important in determining the age of cloud droplets created by the upslope motion. This age Langmuir considers to control very largely the drop size (see page 498).

The number n of drops per cm.^{3}, deduced from d_{vm} and w, is given by Langmuir as

$$n = 0{\cdot}22(55 - \mathrm{T})\,\mathrm{V}(10w)^{-0{\cdot}23}$$

or

$$n = 0{\cdot}32(70 - \mathrm{T})\,\mathrm{V}d_{vm}^{-0{\cdot}70}$$

These equations fit the data for n and V quite well, but the correlation between n and w (or n and d) and between n and T is poorer.

The total liquid water content, however dispersed, of cloud is of great importance in itself, and is, of course, deducible from drop-size distribution curves taken from measured volumes of cloud. But the method is obviously not an accurate one, particularly in view of the difficulties attending the measurement of drop-size distribution curves. Measurements of rime deposition on cylinders will also, as we have seen, provide the water content, but this method is restricted as to temperature. There is, therefore, much point in making direct measurements of water content, but even in this apparently simple procedure the difficulty turns out to be considerable (several hundred per cent. error is readily incurred) and we still do not possess representative values of water (or ice) content over the range of meteorological conditions in different types of

cloud. Radford, in the Houghton and Radford paper referred to earlier, has described a fog-sampling apparatus, consisting essentially of a filter through which the air is aspirated at an appropriate speed. The filter is surrounded by a guard ring five times the diameter of the filter in order to ensure the absence of centrifuging of droplets from the sampled air. Radford gives a few values of water content in sea fog, and in cloud on Mount Washington, ranging from about 0·01 to 1 gm./m.^{3}, but no correlation is attempted with the prime meteorological factors. Water contents up to 5 gm./m.^{3} have been reported (Lacey, *Bull. Amer. Met. Soc.*, **21**, 357, 1940), and such values are probably by no means exceptional in precipitating clouds where, however, a majority of the water is likely to be contained in drizzle and raindrops above the limit of 100μ normally taken as the upper limit of cloud-drops proper.

3. Theoretical Considerations on the Size Distribution and Growth of Cloud Drops

Schumann (*Quart. J.R. Met. Soc.*, **66**, 195, 1940) appears to be the only worker so far to have seriously tackled the problem of the theoretical form of the drop-size distribution curve, as opposed to the mean diameter merely or some other specification of the effective size of cloud droplets. (The problem is not, however, new in regard to dispersed systems in general.) He assumes that, by virtue of Brownian motion, turbulence and differential rates of fall of drops under gravity, collisions between the drops occur leading to coalescence in all cases. It is, in fact, by no means certain that collision always leads to coalescence, but the assumption is a natural one to make in an initial attack upon the problem. He further assumes in the first instance that the frequency of collision is independent of the size of the drops, an assumption which Schumann realises to be rather inadequate. The first assumption leads, of course, to the result that the average size of the drops increases with time and the second then leads to

$$n(v) = \frac{N_0^2}{V(1 + pt)^2} \exp\left\{- \frac{N_0 v}{V(1 + pt)}\right\} \quad . \quad . \quad (1)$$

or $$n(v) = (V/\bar{v}^2) \exp\{- v/\bar{v}\} \quad . \quad . \quad . \quad . \quad (1a)$$

where $n(v)$ is the number of drops per cm.^{3} of volume v.
N_0 is the total initial number of drops per cm.^{3}.
t is the time.
V is the total volume of water per cm.^{3} of air.
$\bar{v}$ is the average volume of drops.

and $p = KN_0/2$ where K is the collision frequency constant, *i.e.* the collision frequency between drops of volumes v_r, v_s per unit concentration of drops of each size, assumed independent of v_r, v_s,

for an assumed initial distribution

$$n_0(v) = \frac{N_0^2}{V} \exp\{-N_0 v/V\} \quad . \quad . \quad . \quad (2)$$

Schumann then goes on to show that equations (1, 1*a*) are likely to be valid after a sufficiently long time, whatever be the initial distribution, but he is only able to supply a formal proof for the case when the drops are initially all of equal size—a very different distribution from that given by (2).

Corresponding to (1), Schumann gives for the drop-radius distribution

$$n(r) = \frac{3r^2 N_0^2}{R^3(1+pt)^2} \exp\left\{-\frac{N_0 r^3}{R^3(1+pt)}\right\} \quad . \quad . \quad (3)$$

where $n(r)$ is the number of drops per cm.^{3} of radius r and $4\pi R^3/3 = V$, and for the volume-distribution curve (see para. 2)

$$U(r) = \frac{20\pi N_0 r^5}{3r_{m^3}(1+pt)} \exp\left\{-\frac{5r^3}{3r_{m^3}}\right\} \quad . \quad . \quad . \quad (4)$$

where $U(r)$ is the fraction of water occupied by drops in the range r to $r + dr$, and $r_m\left(= \left(\frac{5\bar{v}}{4\pi}\right)^{\frac{1}{3}}\right)$ is the radius at which the volume-distribution curve attains a maximum.

Equation (4) is compared with Houghton and Radford's (*loc. cit.*) three published distribution curves, and there is excellent agreement with one of these (the one which, on the basis of Langmuir's analysis, is likely to be the most reliable) and somewhat poorer agreement in two other cases. This, however, is not an absolute test of the theory, and Schumann proceeds to investigate whether coalescence by collision adequately accounts for the actual size of drops. He shows first that collision due to Brownian motion is outweighed by collision due to differences in terminal velocity of fall (Stokes' law regime) for r_m greater than about 3 μ, the absolute law of growth under Brownian motion being

$$r_m = 0{\cdot}0025(Vt)^{0{\cdot}4}$$

and under coalescence due to differential rates of fall

$$r_m = \frac{}{1 - 3{\cdot}23 \times 10^5 \mathrm{V} t\, r_0} \quad \text{or} \quad t = 3{\cdot}1 \times 10^{-6} \frac{r_m - r_0}{\mathrm{V} r_0\, r_m}$$

where $r_m = r_0$ at $t = 0$.

Combining these two laws of growth the figures of Table 1 are obtained for the time of growth from negligibly small drops up to a maximum of 15 μ (limit of Stokes' Law) when V = 1 cm.^{3}/m.^{3}

TABLE 1

TIMES OF GROWTH OF DROPS TO SPECIFIED r_m FOR V = 1 cm.^{3}/m.^{3}

r_m (μ)	t (min.)	r_m (μ)	t (min.)	r_m (μ)	t (min.)
1	5·3	6	127	11	165
2	28	7	138	12	169
3	61	8	148	13	172
4	90	9	155	14	175
5	111	10	161	15	178

Schumann rightly regards these times as excessive, particularly for growth up to about 8 μ, bearing in mind that the water content is often only about one-tenth of the assumed value. The reason is likely to be found in the neglect of evaporation and condensation processes considered quantitatively by Langmuir (see below).

Schumann concludes his treatment by a consideration of the case when the collision frequency is a linear function of the drop size, and arrives at an integral equation for the distribution function which has so far defied solution.

It will be noted that Schumann treats throughout with a cloud (or fog) of constant water content, and it is not immediately evident how a change in V corresponding to the growth of a cloud or fog will modify his results.

Langmuir (*loc. cit.*) has developed a "time-of-rise" theory, or more simply an age-theory, in connection with his analysis of the Mount Washington riming data, which, he claims, gives an excellent explanation of the drop sizes observed in those experiments (see para. 2) and which he believes may be extended to cover all stages in the growth of a cloud up to the rain or snow stage. This theory is based on the excess vapour pressure at a curved surface (Kelvin effect), as a result of which an initial distribution of drop-diameters becomes changed, due to evaporation from the smaller drops and condensation on the larger, with a concurrent decrease in concentration of the drops. Because the relative excess vapour pressure over a curved surface is so small for drops greater than about 10^{-5} cm.

diameter, it has commonly been supposed that the effect is of no practical importance once droplets reach this size. That is true as far as evaporation in an unsaturated atmosphere is concerned, but in a near-saturated or only slightly super-saturated atmosphere, such as occurs in clouds, Langmuir considers the effect to be predominant up to droplet diameters of about 30 μ, and this limit of size probably takes in a majority of non-precipitating clouds.

Langmuir first develops the equation of evaporation of, or condensation on a droplet, *viz.*

$$r\,dr/dt = -\frac{\mathrm{MD}\Delta e}{\rho_w \mathrm{RT}} \quad . \quad . \quad . \quad (5)$$

where r is the radius at time t, M is the molecular weight of water vapour, D the coefficient of diffusion of water vapour, ρ_w the density of water ($= 1{\cdot}0$), R the universal gas constant, T the temperature and Δe the excess vapour pressure at the surface of the drop (in the cases considered here, of excess due to curvature only, $\Delta e = \frac{2\mathrm{M}\gamma}{\rho_w \mathrm{RT}}\frac{e}{r}$ where γ is the surface tension and e the saturation vapour pressure at temperature T). When r is less than about 10^{-5} cm. and comparable with the mean free path λ of molecules Langmuir's formula for evaporation in high vacuum is introduced in (5), together with the above form for Δe, giving an integration for the life t of a drop of radius r in a saturated atmosphere *

$$t = \frac{1}{2}\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\left(\frac{\mathrm{RT}}{\mathrm{M}}\right)^{\frac{3}{2}}(\rho_w r)^2/(e\gamma)$$

$$= 6{\cdot}21 \times 10^9\, \mathrm{T}^{\frac{3}{2}}\, r^2/(e\gamma) = \alpha r^2, \text{ say} \quad . \quad . \quad (6)$$

(Inserting numerical values, the life of a particle of 10^{-5} cm. radius in saturated vapour at $-10°$ C. is 0·012 sec.) When the droplet is greater than 10^{-5} cm. diameter (5) may be integrated immediately, on substituting for Δe in terms of r, and gives

$$t = \frac{1}{6}\mathrm{D}\gamma e\left(\frac{\rho_w \mathrm{RT}}{\mathrm{M}}\right)^2(r^3 - r_1^3) = \beta(r^3 - r_1^3), \text{ say} \quad . \quad . \quad . \quad (7)$$

where t is the time taken for the drop to decrease from r to r_1 ($r_1 \approx \lambda$). For most purposes r_1^3 may be neglected *cf.* r^3, and we then have, as an example, the life of a droplet of 1 μ radius at $-15°$ C. $\doteq 6{\cdot}2$ sec., whereas for $r = 10\ \mu$, $t = 6200$ sec.

* This procedure neglects the effect of the hygroscopic nucleus on which the drop is formed and so t as given is an underestimate; in fact, the drop will not completely evaporate in a saturated atmosphere (see Simpson, *Quart. J. R. Met. Soc.*, **67**, 106, 1941). But this error is not likely to affect seriously Langmuir's later conclusions on cloud development.

Langmuir now applies formulæ (6) and (7) to a cloud of droplets, making the assumption that the relative size-distribution function remains unchanged during the process of drop disappearance and growth. This condition is not likely to be strictly fulfilled, but the effects of curvature are not in fact sensitive to moderate changes in the distribution function. It is also satisfactory to apply (6) and (7) to the cloud as distinct from individual drops, since the drops in all clouds are on average widely separated (*cf.* para. 2) and do not, therefore, interfere except indirectly with the evaporation process at any one drop. The first assumption leads to the result that the fraction of drops disappearing in unit time should vary inversely as the life t of the drops of average size. Expressed formally

$$\frac{d}{dt}(\log n) = -\frac{1}{kt} = -\frac{1}{k\alpha r^2} \text{ in the range of } r \text{ for (6)} \quad . \quad . \quad (8)$$

and

$$= -\frac{1}{k\beta r^3} \qquad \text{in the range of } r \text{ for (7)} \quad . \quad (9)$$

where k is a constant depending on the distribution function, of order unity, and to be determined from experimental data.

In air expanding adiabatically at a uniform rate, with nuclei sufficient to prevent more than infinitesimal supersaturation, the total water content increases approximately linearly with time from the instant of saturation. Thus $nr^3 = ct$ where c is a constant determined by the rate of formation of water, *i.e.* by the temperature and vertical velocity. Differentiating this equation logarithmically and inserting (8) gives

$$r^2 = \frac{2t}{k\alpha} + \mathrm{A}\,t^{\frac{2}{3}} \;.\;.\;.\; r < 10^{-5} \text{ cm.} \quad . \quad . \quad (10)$$

where A is an integration constant, while inserting (9) gives

$$r^3 = \frac{t}{k\beta} \log \mathrm{B}\,t \;.\;.\;.\; r > 10^{-5} \text{ cm.} \quad . \quad . \quad (11)$$

where B is a further constant of integration.

For very small t equation (10) gives $r \propto t^{\frac{1}{3}}$, which with $nr^3 = ct$ makes n independent of time and for these small t

$$n = n_0, \text{ say, } = c/\mathrm{A}^{\frac{3}{2}}$$

Introducing this in (10)

$$r^2 = \frac{2t}{k\alpha} + \left(\frac{ct}{n_0}\right)^{\frac{2}{3}} \;.\;.\;.\; r < 10^{-5} \text{ cm.} \quad . \quad . \quad (12)$$

If n_0 is very large, *i.e.* if the nuclei are very numerous, or sufficient to make the second term of (12) negligible

$$r^2 = \frac{2t}{k\alpha} \;.\;.\;.\; r < 10^{-5} \text{ cm.} \quad . \quad . \quad . \quad (12a)$$

The constant B in (11) may be evaluated by making the two solutions (10) and (11) continuous for $r = r_1 = 10^{-5}$ cm. at $t = t_1$ and

$$r^3 = r_1^3\, t/t_1 + \frac{t}{k\alpha} \log t/t_1 \quad . \; . \; . \quad r > 10^{-5} \text{ cm.} \qquad (13)$$

or

$$ct/n_1 + \frac{t}{k\alpha} \log t/t_1 \qquad r > 10^{-5} \text{ cm.} \qquad (13a)$$

If the nuclei are initially unlimited, ct/n_1 is negligible *cf.* r^3 and (13*a*) reduces to

$$r^3 = \frac{t}{k\alpha} \log t/t_1 \quad . \; . \; . \quad r > 10^{-5} \text{ cm.} \qquad (13b)$$

where, from (12*a*) with $t = t_1$ for $r = 10^{-5}$ cm.,

$$t_1 = 5 \times 10^{-11} k\alpha \qquad (14)$$

Equations (13) apply to the main body of the cloud, the time t being the time the air has taken to rise from the base of the cloud to any level under consideration. As the air rises the concentration of droplets decreases while the radius increases. The figures of Table 2 indicate the scale of the process. These are to be contrasted with the figures given in Table 1 based on growth by coalescence.

TABLE 2

RADIUS OF WATER DROPLETS IN MICRONS AS A FUNCTION OF TIME AND TEMPERATURE

Based on $k = 1$; for other k multiply by $1/k^{1/3}$.)

T (° C.)	t (sec.)									t_1(sec.)
	1	10	40	80	120	300	600	1200	3600	
20	2·31	5·48	9·13	11·75	13·60	18·9	24·2	31·0	45·9	0·0009
10	1·83	4·35	7·29	9·38	10·86	15·16	19·4	24·9	36·8	0·0016
0	1·42	3·42	5·70	7·35	8·55	11·9	15·2	19·4	29·1	0·0030
− 10	1·07	2·60	4·37	5·65	6·56	9·17	11·8	15·2	22·6	0·0060
− 20	0·78	1·93	3·26	4·24	4·90	6·86	8·9	11·4	17·0	0·0127

For application to the rime measurements on Mount Washington it is necessary to determine t in each case. Langmuir takes $t = h/SV$ where h is the height of the level of observation above the cloud base, S the slope of the mountain ($= 0{\cdot}32$) and V the wind speed, realising that conditions may sometimes arise when the age of the drops is not adequately obtained by this simple formula which gives, rather, a lower limit. The height h is given by the water content w of the cloud (all condensed water is assumed to be retained in the rising air) and the temperature at the level of observation

according to thermodynamic calculations made by Langmuir or as readily deduced from a tephigram or other thermodynamic chart, and one then finally obtains

$$t \propto \frac{w}{V}$$

the factor of proportionality being dependent on temperature. From t the theoretical radius is obtained from Table 2, apart from an uncertainty regarding the appropriate value of k, overcome by making k times the mean theoretical value of r^3 equal to the mean observed value of r^3; this gave $1/k^{1/3} = 1{\cdot}25$ ($k = 0{\cdot}51$).

The individual values of r thus determined were correlated logarithmically with the individual observed values, and a coefficient of 0·955 resulted when a small fraction of the observations were excluded as being clearly unrepresentative of the general run—these excluded values are likely to have arisen by the sampling of cloud which did not reach the point of observation directly from the base of cloud, as evidenced by excessively large radii. The agreement between theory and observation for the majority of cases is undeniably excellent, while the empirical relations which were deduced from the riming data, and which have already been given in para. 2 (*q.v.*), are also in excellent agreement with the theory, though there is a formal difference due to the methods of analysis. Langmuir points out that other theories advanced in the past are not consistent with his empirical relations deduced from riming.

Langmuir promises a development of his theory to take account of the later stages of growth, where in the higher cloud levels w becomes large and the drops begin to fall at an appreciable rate through the air, so that equation (5) is no longer applicable. This stage is accompanied by growth by accretion according to laws similar to those governing the formation of rime on cylinders, and when certain rather critical conditions are reached the accretion is so rapid that the cloud produces drizzle or rain. He suggests that a quantitative theory of rain formation is now in sight. This speculation is of interest in relation to Simpson's (*loc. cit.*) conclusion that the Bergeron theory of rain formation, which demands the coexistence of ice crystals and water droplets, is not in fact necessary when the vertical velocity is large, though it is no doubt often in evidence.

We have described Langmuir's theory in some detail because of its manifest potential importance to a fundamental meteorological problem. Findeisen (*Met. Z.*, **56**, 453, 1939) has also written on the theory of evaporation of cloud droplets and has extended the

work to the evaporation of drizzle and rain, obtaining a number of important conclusions which have been summarised by Simpson (*loc. cit.*). In this he has made use of Frössling's (*Beitr. Geophys.*, **52**, 170, 1938) detailed observations on the evaporation of drops (0·1 mm. $< r <$ 0·9 mm.) beyond the Stokes' Law regime. But Findeisen neglected the effect of curvature and, while this does not materially affect his conclusions regarding evaporation of small droplets in an unsaturated atmosphere, it means that he missed the important conclusions of Langmuir and misinterpreted his own results in relation to rain formation (Findeisen, *Met. Z.*, **56**, 365, 1939). On this subject readers are also referred to a very comprehensive paper by Fuchs (*Phys. Z., Soviet Union, Kharkov*, **6**, 224, 1934) on evaporation and condensation of small droplets, a paper which has probably been overlooked by many meteorologists.

4. Investigation of Clouds by Radar

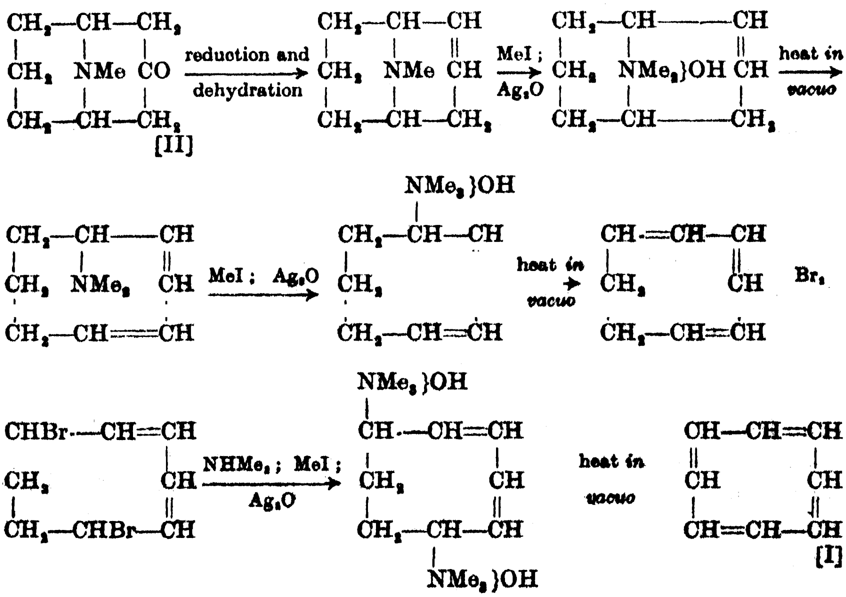
An important additional tool in the investigation of clouds has emerged during the war with the development of centimetric radar. The nature of the echoes obtained from clouds in relation to their structure has been summarised by Sheppard (*Nature*, **157**, 860, 1946) and will be dealt with in more detail in papers by Appleton, Ryde, Westwater and Ross in *Report on Meteorological Factors in Radio Wave Propagation* (R. Met. Soc. and Phys. Soc., 1947). (See also Maynard, *J. Met.*, **2**, 214, 1945; Bent, *ibid.*, **3**, 78, 1946; Miller, *Bull. Amer. Met. Soc.*, **28**, 19, 1947). The intensity of the echo from a cloud composed of true cloud droplets (d of order 10 μ) is theoretically proportional to nd^3, *i.e.* to the water content, but for larger drops composing drizzle and rain is proportional nd^6. Thus radar provides a very sensitive detector of the presence of larger drops.

A complete correlation between radar echoes and cloud structure has not so far been made because, as is evident, we lack the data on cloud particle concentration and diameters in thoroughly representative conditions such as are not likely to be obtained on any mountain station. But it appears likely that with a little more knowledge there will be a twofold advance—in gaining a greater understanding of centimetric radio scattering and in applying this in turn to the examination of certain very important aspects of cloud structure, particularly of cumulonimbus cloud where the water content and drop diameters usually provide good echoes.

ORGANIC CHEMISTRY. By A. W. Johnson, Ph.D., A.R.C.S., The University, Cambridge.

*CYCLO*OCTATETRAENE.—Information has recently been released by the Ministry of Supply that a method for the polymerisation of acetylene to *cyclo*octatetraene had been developed by Reppe and his co-workers in the Ludwigshafen laboratories of I.G. Farben. *Cyclo*octatetraene is thus transformed from a text-book curiosity to a fairly readily available intermediate.

The original preparation of *cyclo*octatetraene [I] was the outcome of a brilliant, though laborious, synthesis by Willstätter and his co-workers (*Ber.*, 1911, **44**, 3442) starting from ψ-pelletierine [II]:



By this method some 3–4 g. of *cyclo*octatetraene was prepared which was described (see also *Ber.*, 1913, **46**, 517) as a pale yellow liquid, b.p. 42·2–42·4°/17 mm. The hydrocarbon appeared to possess no aromatic stability; it was readily oxidised by permanganate or atmospheric oxygen and readily combined with bromine and hydrogen bromide. Hydrogenation of the product gave *cyclo*octane, m.p. 6·5°, which was oxidised by nitric acid to suberic acid. On this evidence, the above structural formula was advanced and no further experimental work was carried out until 1939 when a number of suggestions were made (summarised by Baker, *J. Chem.*

Soc., 1945, 258) that Willstätter's hydrocarbon might be styrene on the grounds of similarity between the chemical and physical properties of the two hydrocarbons. These criticisms disregarded the formation of *cyclo*octane on hydrogenation and the subsequent oxidation to suberic acid—definite proof of the presence of a certain amount of *cyclo*octane in the hydrogenation product.

The recent work of Reppe (B.I.O.S. 137 and supplement, "*Cyclo*polyolefines"; B.I.O.S. 352, "*Cyclo*polyolefines") leaves no doubt that the product from the polymerisation of acetylene is chemically identical with that originally described by Willstätter, and is *cyclo*octatetraene. The polymerisation was effected in a solvent, *e.g.* tetrahydrofuran, and in the presence of a catalyst, anhydrous nickel cyanide. The presence of a drying agent, *e.g.* calcium carbide, was also claimed to be advantageous. The reaction was effected under pressure and at a temperature of about 80° and yielded a mixture of *cyclo*polyolefines :

*cyclo*octatetraene . . .	b.p. 142–143°/760 mm., golden yellow
$C_{10}H_{10}$	b.p. 190–195°/760 mm., deep yellow
$C_{12}H_{12}$	b.p. 230–235°/760 mm., light yellow
azulene	m.p. 99·5°, deep blue

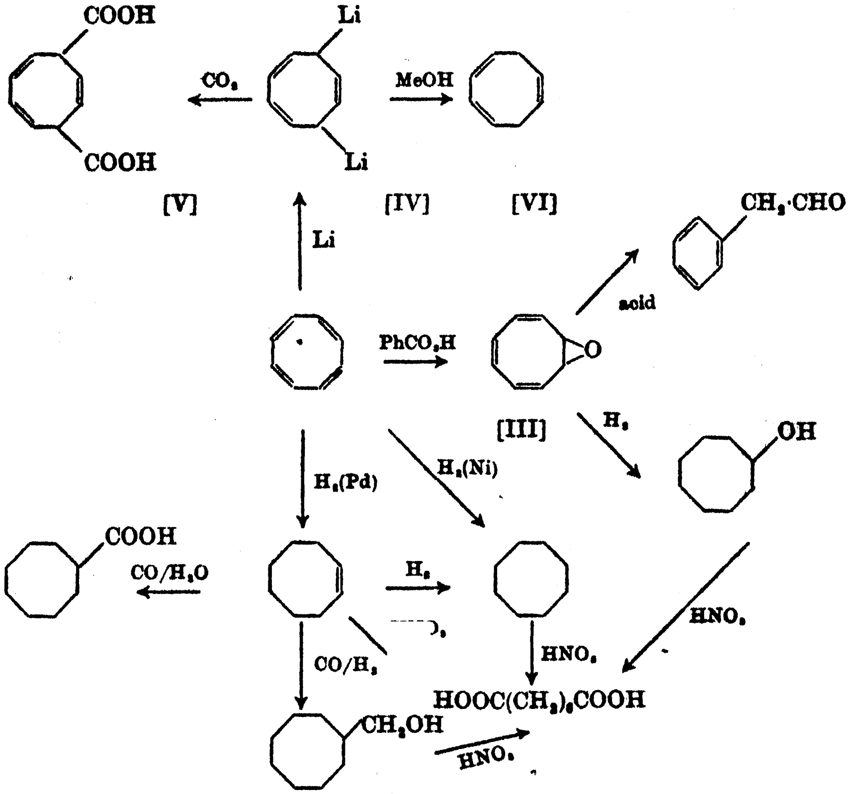
No indication was given of the formation of any aromatic hydrocarbons which is surprising as *cyclo*octatetraene has a higher energy content than benzene.

	Heat of Combustion (K cal./mol.).	Heat of Formation (K cal./mol.).
Benzene	783	− 12·4
*Cyclo*octatetraene . .	1069	− 40

The proportion of the higher polymers was favoured by higher reaction temperatures, but the exact structures of these polymers is still in doubt. Hydrogenation of $C_{10}H_{10}$ does not give *cyclo*decane and further oxidation does not give sebacic acid which rules out any possibility of a *cyclo*decapentaene structure. Vinyl*cyclo*octatetraene is a further possibility but more experimental evidence is required on this point. Very little data is available on the structure of the $C_{12}H_{12}$ isomer, but it is very unlikely to be *cyclo*dodecahexaene as suggested.

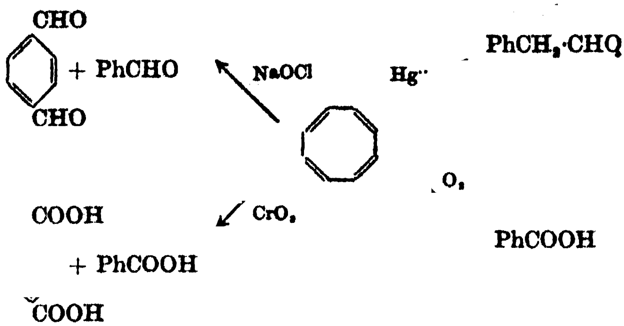
As was observed by Willstätter, *cyclo*octatetraene shows no aromatic character. It is fairly readily oxidised by air to an amorphous white solid, is easily attacked by oxidising agents and

easily adds halogens. It behaves as a typical diene in Diels-Alder syntheses and can be dimerised on heating. Reactions of *cyclo*-octatetraene where the 8-ring is preserved are as follows:



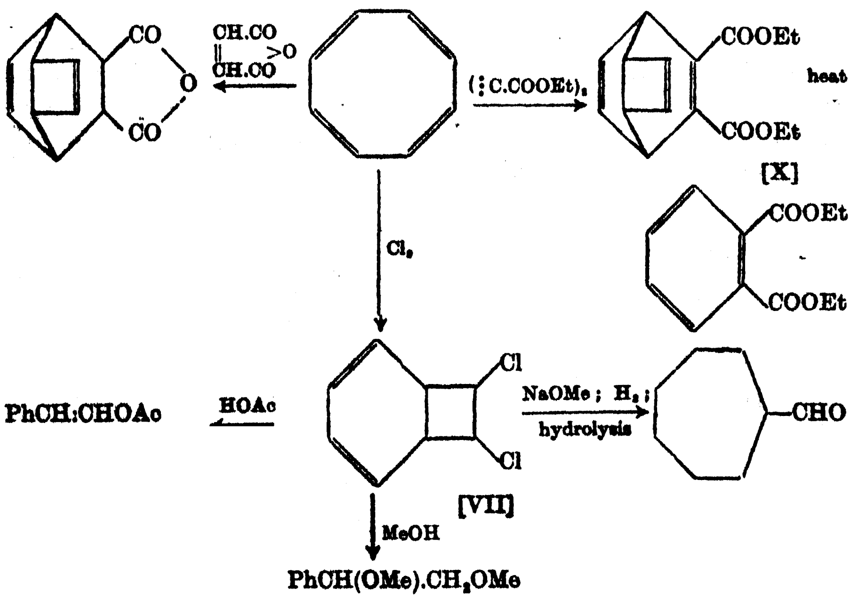
Hydrogenation yielded successively *cyclo*octene and *cyclo*octane, both of which may be oxidised to suberic acid with nitric acid. The formation of *cyclo*octylcarbinol by the action of carbon monoxide and hydrogen on either *cyclo*octatetraene or *cyclo*octene and the conversion of *cyclo*octene to *cyclo*octylcarboxylic acid are interesting applications of the recently developed carbon monoxide reactions. The action of per-acids on *cyclo*octatetraene gave the monoxide [III] which may be hydrogenated to *cyclo*octanol or re-arranged, quantitatively, by the action of dilute acids to phenyl-acetaldehyde. Lithium was claimed to add 1 : 4-to *cyclo*octatetraene and the dilithium adduct [IV] could be carboxylated to the corresponding *cyclo*octatriene dicarboxylic acid [V] or hydrolysed to the *cyclo*octatriene [VI].

*Cyclo*octatetraene may also be converted to a variety of aromatic compounds :

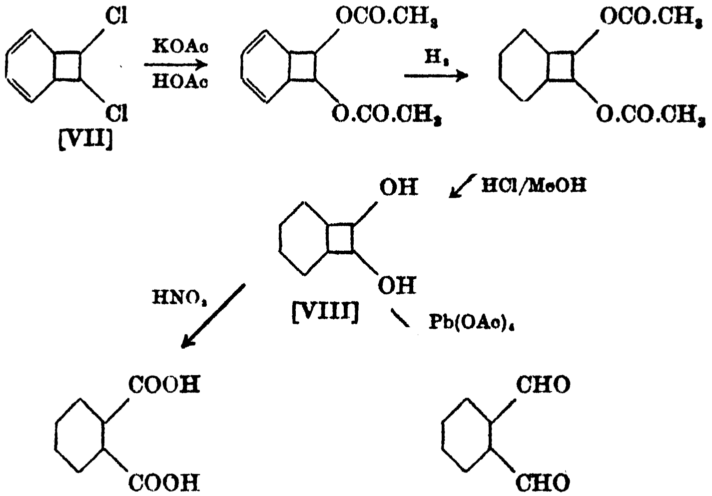


Treatment of an aqueous suspension of *cyclo*octatetraene with mercuric salts, *e.g.* sulphate, caused rearrangement to phenylacetaldehyde in good yield while substitution of alcohol or acetic acid as the solvent led to the corresponding diethylacetal or phenylethylidene diacetate respectively. Aerial oxidation of *cyclo*octatetraene over a vanadium pentoxide catalyst gave benzoic acid ; oxidation with sodium hypochlorite gave a mixture of benzaldehyde and terephthaldialdehyde and chromic oxidation yielded terephthalic acid together with some benzoic acid. The yields obtained from these oxidation experiments were not quoted, but it is unlikely that they were high.

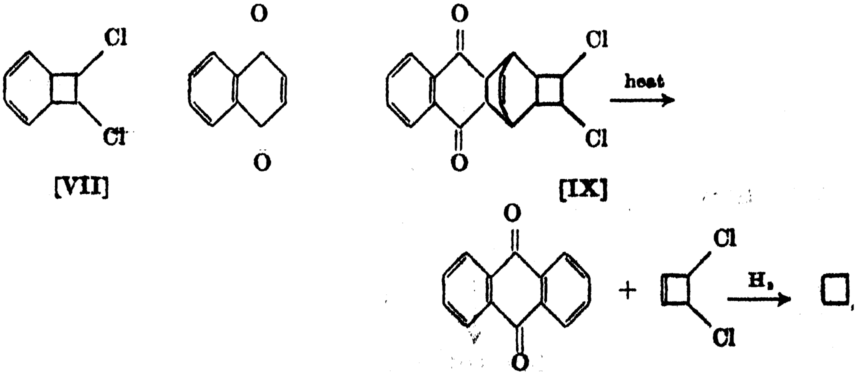
A further series of reactions of *cyclo*octatetraene involves its conversion to derivatives of [0 : 2 : 4]*bicyclo*-2 : 4 : 7-octatriene :



These addition reactions include the action of halogens, and the dichloride, obtained by the action of sulphuryl chloride in chloroform solution, was proved to be 7 : 8-dichloro-[0 : 2 : 4] *bicyclo*-2 : 4-octadiene [VII]. Thus, conversion to the corresponding diacetate followed by hydrogenation and hydrolysis gave a saturated glycol [VIII] from which *cis*-hexahydrophthalic acid was obtained by nitric acid oxidation and *cis*-hexahydrophthalaldehyde on oxidation with lead tetracetate, thus indicating the position of the original chlorine atoms.



Further evidence for the presence of the 4-membered ring was afforded by the Diels-Alder reaction with 1 : 4-naphthoquinone when the adduct [IX] was obtained which decomposed on heating to give anthaquinone and 1 : 2-dichloro-3-*cyclo*butene, m.p. 44°. Catalytic hydrogenation of this dichloro compound gave *cyclo*butane.



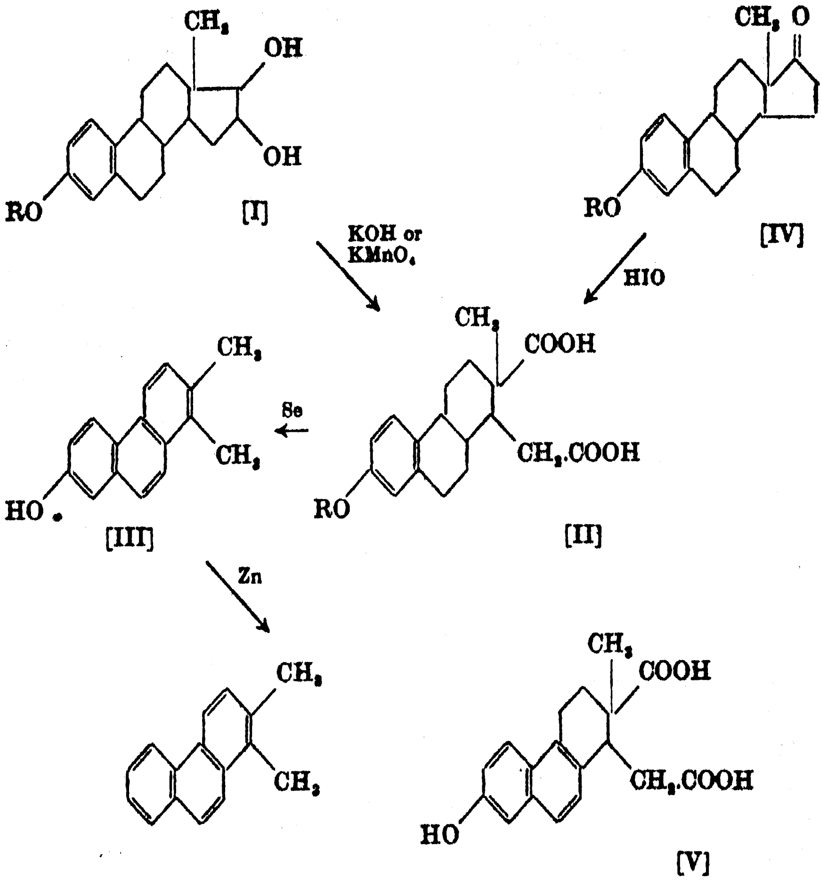
Further rearrangements were observed in certain of the reactions of [vii], *e.g.* acetic acid gave styryl acetate; methanol gave $\alpha\beta$-dimethoxyethyl benzene and sodium methoxide yielded a product which on hydrogenation and acid hydrolysis gave cycloheptyl aldehyde.

*Cyclo*octatetraene also gave Diels-Alder adducts containing 4-membered rings, *e.g.* with maleic anhydride, acrylic acid, quinones and acetylenedicarboxylic ester. A further proof of the structure of the latter adduct [x] was afforded by the formation of phthalic ester by the action of heat. On heating *cyclo*octatetraene under reflux at atmospheric pressure, a mixture of polymers are formed, from which two isomeric dimers were isolated. The precise structure of these dimers is still obscure, although it is possible that they are formed by a diene-type synthesis.

A wide range of *cyclo*octane derivatives may thus be obtained, as well as a number of other hitherto inaccessible compounds, using *cyclo*octatetraene as the starting-point, and as the German work was interrupted before completion it may be expected that there will be further communications on the chemical and physical properties of this intriguing hydrocarbon.

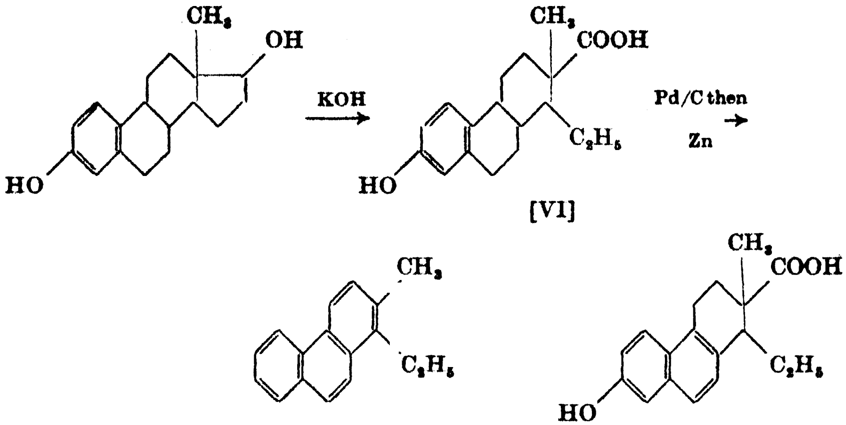
Œstrogenic Carboxylic Acids.—An interesting series of papers by Miescher and his collaborators has appeared during the last three years (*Helv. chim. Acta*, 1944, **27**, 1727; 1945, **28**, 156, 991, 1342, 1506; 1946, **29**, 449, 586, 859, 1071, 1231, 1889, 1895; 1947, **30**, 413, 544, 550. *Experientia*, 1946, **2**, 237, 409) concerning the preparation and properties of certain substituted hydrophenanthrenecarboxylic acids obtained by degradation of œstrone and equilenin. These acids have proved to be highly active œstrogenic compounds.

The work began with a re-examination of some earlier degradations of œstriol. Marrian and Haslewood (*J. Soc. Chem. Ind.*, 1932, **51**, 277T) and Doisy and his co-workers (*J. Biol. Chem.*, 1933, **99**, 327) had shown that a C_{18} dicarboxylic acid could be obtained by fusing œstriol [i] with potassium hydroxide or by the action of permanganate on the corresponding 3-methyl ether. The structure of this acid, now named marrianolic acid [ii; R = H] was determined by Butenandt *et al.* (*Ber.*, 1933, **66**, 601), who showed that it could be dehydrogenated to a dimethylphenanthrol [iii] and thence converted by treatment with zinc dust to 1 : 2-dimethylphenanthrene.



Miescher has now shown that marrianolic acid may be more readily obtained by a hypoiodite oxidation of œstrone benzyl ether [IV; R = $PhCH_2$], followed by hydrogenolysis of the benzyl group. Similar treatment of equilenin benzyl ether gave bisdehydromarrianolic acid [V].

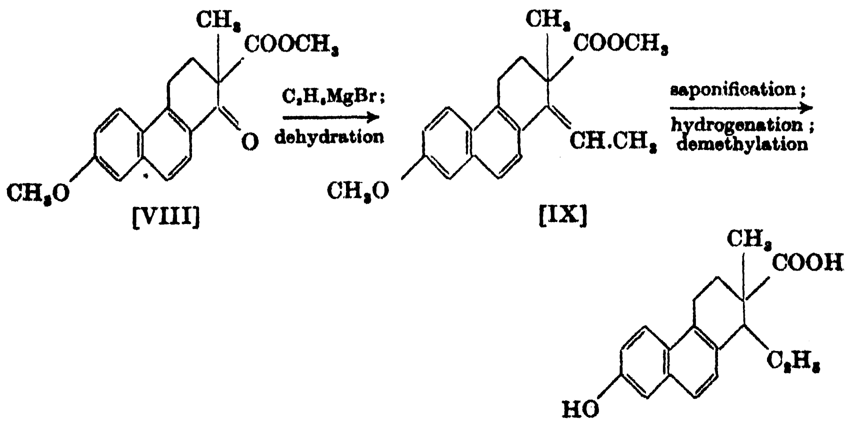
A further acid, doisynolic acid [VI], was obtained by fusion of œstradiol with potassium hydroxide at 275°, and the structure was proved by a similar degradation to that effected with marrianolic acid, the final product being 1-ethyl-2-methylphenanthrene. Doisynolic acid produced œstrus in rats by the subcutaneous application of 0·7–1·0 γ (œstrone 0·7–1·0 γ) or by an oral administration of 1·5 γ. The corresponding bisdehydrodoisynolic acid (VII] was obtained from equilenin by a similar alkaline fusion.



[VI]

[VII]

[VII] was separated into the two geometrical isomers—the normal (C_1 alkyl *trans* to C_2 carboxylic acid) and the iso (C_1 alkyl *cis* to C_2 carboxylic acid) of which the normal form produced œstrus in subcutaneous doses of 0·1–0·15 γ or oral doses of 0·1–0·2 γ while the iso form was inactive in doses of $<$ 100 γ. Bisdehydrodoisynolic was first synthesised from methyl 1-keto-2-methyl-7-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene-2-carboxylate [VIII], an intermediate already described by Bachmann *et al.* (*J. Amer. Chem. Soc.*, 1940, **62**, 824) in their elegant synthesis of equilenin, by a Grignard reaction with ethylmagnesium bromide followed by dehydration, saponification, hydrogenation and demethylation.



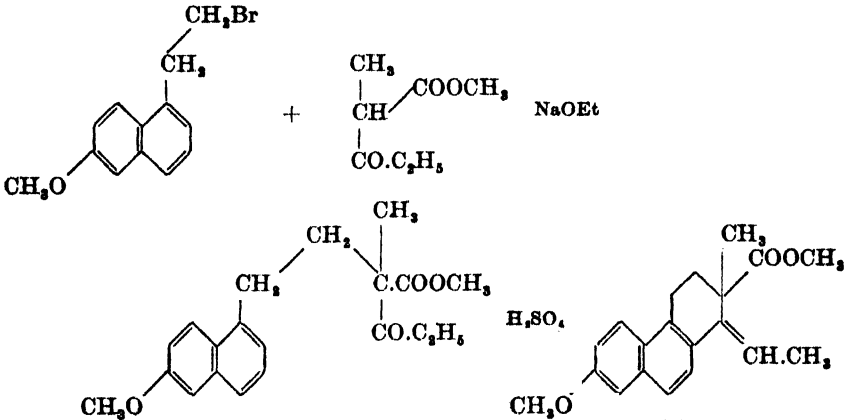
[VIII]

[IX]

[VII]

The *rac.* acid so produced was resolved with *l*-menthol. The above synthesis was later replaced by a simpler method whereby 1-(β-bromoethyl)-6-methoxynaphthalene was condensed with α-propionyl

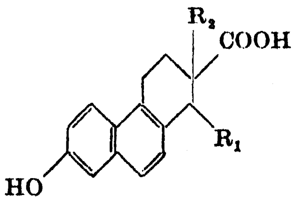
propionic ester to give a product which was cyclised by treatment with sulphuric acid to yield [IX] and thence, as before, to [VII].



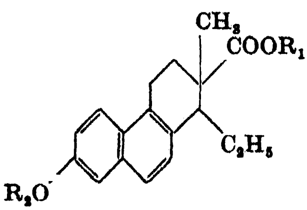
[IX]

A large number of variations of the bisdehydrodoisynolic acid molecule have been synthesised, including examples of the following types. The list of activities is not exhaustive and reference should be made to the originals for full details:

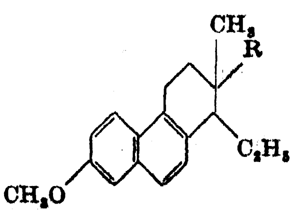
AMOUNT REQUIRED (γ) FOR ŒSTRUS PRODUCTION IN RATS BY SUBCUTANEOUS INJECTION



R_1	R_2	*iso*-Series.	*n*-Series.
CH_3	CH_3	70	0·1–0·2
C_2H_5	C_2H_5	> 1000	0·3–0·5
C_2H_5	*n*–C_3H_7	—	0·2
C_2H_5	CH_3	300–500	0·1–0·15
H	H	Short œstrus at 200	



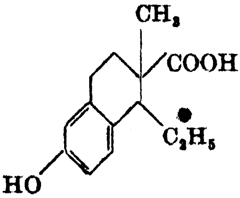
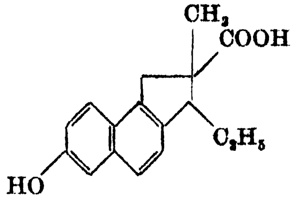
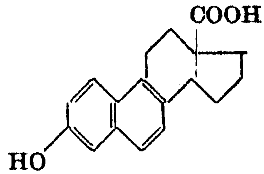
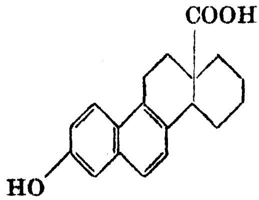
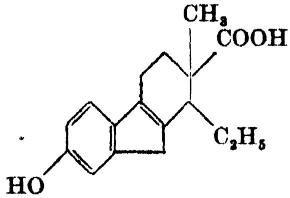
R_1	R_2	*rac.*-Series.



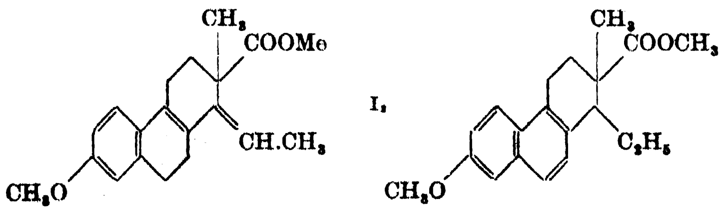
R	*rac.*-Series.
—$CO.CH_3$	1000*
—C_2H_5	1000
—$CO.CH_2OCOCH_3$	300–500*
—$CH_2.COOH$	300–500*

* Double subcutaneous injection.

In addition, examples of the following types have been examined but biological tests are still awaited in certain cases:

Although a synthesis of doisynolic acid has been claimed (Hunter and Hogg, *J. Amer. Chem. Soc.*, 1946, **68**, 1676) the product was amorphous and melted over a wide range, 90–110°. This claim has been refuted by Miescher (*Experientia*, 1946, **2**, 409), who thought that the product of Hunter and Hogg was more likely to be a mixture of acids in varying stages of hydrogenation. In support of this statement, Miescher has outlined some of his own experiments directed towards the synthesis of doisynolic acid where an unexpected facile rearrangement to the bisdehydrodoisynolic series was observed (see also *Helv. chim. Acta*, 1946, **29**, 1889; 1947, **30**, 550) *e.g.*



Further work on the synthesis of doisynolic acid types may be expected in future publications.

GENERAL AND PHYSICAL CHEMISTRY. By J. W. Smith, D.Sc., Ph.D., F.R.I.C., Battersea Polytechnic.

Structure of the Boron Hydrides and Related Compounds.—Theories regarding the structures of the hydrides of boron have for some time aroused a very keen general interest amongst chemists, owing to the bearing which they have on the conception of valency and the nature of chemical linkages. The formulæ of the known

compounds of this type, namely B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$, appear to be quite anomalous and are not of the form to be anticipated on the grounds either of the classical picture of the tervalency of boron or on the simple electronic theory of valency.

Thus diborane, B_2H_6, has two valency electrons less than ethane, C_2H_6, which is formally similar to it. Therefore it has insufficient electrons to permit of electron-pair linkings between each hydrogen atom and a boron atom and between the two boron atoms. Similar electron deficiencies occur in the other hydrides, tetraborane, B_4H_{10}, for instance, having four electrons less than butane, C_4H_{10}.

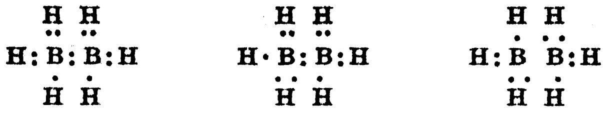
It may be remembered that there have been two main schools of thought regarding the structure of these compounds, the one school accepting the apparent electron deficiency as real, and seeking to explain the stability of compounds in which the octets are not completed, whereas the other school has devised structures with normal electron-pair linkages and with complete octets of electrons around each boron atom.

In leading the first form of approach to the problem, Sidgwick (*The Electronic Theory of Valency*, 1927, p. 103) considered it to be necessary to assume that in B_2H_6 two of the hydrogen atoms are linked to boron atoms by single electron linkages (I), whilst Sugden (*J. Chem. Soc.*, 1927, 1173) and independently Main Smith (*Chem. News*, 1927, **135**, 81) suggested that four of the hydrogen atoms might be linked by single-electron linkages, leaving a four-electron linkage, or double bond, between the two boron atoms (II). The latter structure has the advantage of giving a complete octet of electrons around each boron atom.

$$\begin{array}{ccccccc} & & H & & H & & \\ & & \cdot\cdot & & \cdot\cdot & & \\ H & : & B & : & B & : & H \\ & & \cdot & & \cdot & & \\ & & H & & H & & \end{array} \qquad\qquad \begin{array}{ccccccc} & & H & & H & & \\ & & \cdot & \cdot & \cdot & & \\ H & : & B & : & B & : & H \\ & & \cdot & \cdot & \cdot & & \\ & & H & & H & & \end{array}$$

(I) (II)

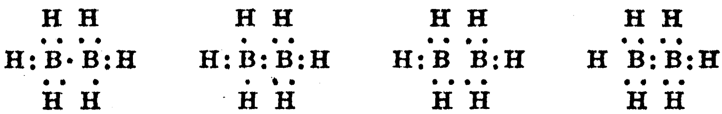
Soon after this period there was developed the theory of resonance, whereby, with certain limitations, when a molecule can exist in two or more forms of equal, or nearly equal, energy, these structures become, so to speak, superimposed upon one another. The resulting structure, therefore, is intermediate between them, being nearest to that of the form of lowest energy, and is more stable than any of the extreme structures which can be formulated in the normal way. This theory caused Sidgwick's view to be extended, since in structure (I) any of the three hydrogen atoms on the left-hand boron atom may be the one which is linked by a single electron, as in (Ia), (Ib), and (Ic), and each of these may be associated with each of the three possible positions of the single-electron linkage on the



(Ia) (Ib) (Ic)

right-hand boron atom, giving altogether nine structures with identical energy. The resulting structure, therefore, will be practically the product of superposing these structures, that is a structure where all the hydrogen atoms are linked to the boron atoms with identical linkages, intermediate between one-electron and two-electron linkages, but approaching more closely to the latter, since each position has two electrons in six of the nine structures and one electron only in the other three.

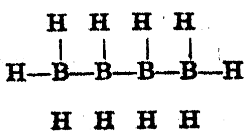
In the later developments of this theory as applied to the boron hydrides, due principally to Pauling and Bauer, there were included also the various forms of the structures wherein a single-electron linkage occurs between the two boron atoms, two single-electron linkages occur on one boron atom, and where " no-electron " linkages occur between the two boron atoms or between a boron atom and a hydrogen atom, as in (III), (IV), (V), and (VI). The no-electron



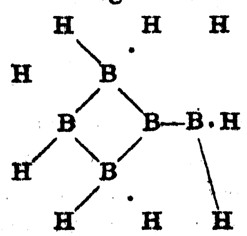
(III) (IV) (V) (VI)

linkage was included to account for the diamagnetic character of B_2H_6, which appeared to be strange if there were two single-electron linkages. However, according to the resonance theory it would only be possible for the no electron forms to participate in the final structure if the spins of the electrons of the single linkages are antiparallel, so that their magnetic affects cancel one another out.

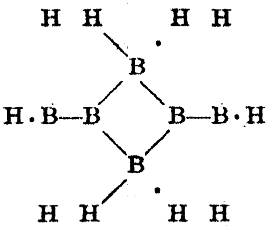
On these bases Pauling built up structures for all the boron hydrides B_4H_{10}, B_5H_9, B_6H_{10}, and $B_{10}H_{14}$ which were regarded as involving the superposition of all the possible variations in the formulæ as given in (VII), (VIII), (IX), and (X), respectively, in which lines represent two-electron linkages and dots single-electron linkages.



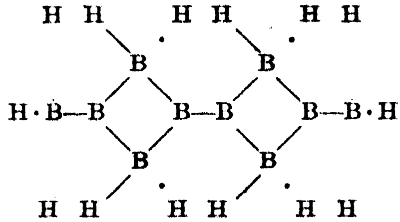
(VII)



(VIII)



(IX)



(X)

A number of difficulties arise, however, in respect of all these formulations which base diborane upon an ethane structure. It has, for instance, been found very difficult to account for the observed Raman and infra-red spectra on a structure of this form. Again, the single electron linkage is definitely known to exist only in the transient H_2^+ particle, which has one electron only, and therefore cannot be compared with the relatively stable boron hydrides. Finally, in spite of the explanation which has been given for the diamagnetism of these compounds, the fact remains that all known boron hydrides contain an even number of electrons, suggesting that all the electrons are actually paired.

The second general school of thought followed the original ideas of Stock, later developed and extended by his collaborator Wiberg, that the boron hydrides can be regarded as electrovalent compounds with structures more closely analogous to the unsaturated hydrocarbons than to the paraffins. Thus B_2H_6 and B_4H_{10} were formulated with structures similar to those of ethylene and butadiene, respectively, but with two and four hydrogen atoms in addition linked by electrovalent linkages (XI) and (XII). Such structures

$$H_2\left[H_2B=BH_2\right] \qquad H_4\left[H_2B=BH-BH=BH_2\right] \qquad \bar{B}H_2\overset{+}{H}:\bar{B}H_2\overset{+}{H}$$

(XI) (XII) (XIII)

appeared to be supported by the fact that the hydrides interact with ammonia to give addition products $B_2H_6,2NH_3$, $B_4H_{10},4NH_3$, $B_5H_9,4NH_3$, and $B_{10}H_{14},6NH_3$, which could be formulated as salts $(NH_4)_2\,B_2H_4$, $(NH_4)_4\,B_4H_6$, $(NH_4)_4\,B_5H_5$, and $(NH_4)_6\,B_{10}H_8$. In addition, it was found that the absorption spectra of B_2H_6 and B_4H_{10} resembled those of ethylene and butadiene rather than those of ethane and butane, whilst additional support was claimed from parachor measurements. An unsaturated character is also indicated by the fact that the hydrides add on alkali metals to give compounds such as $K_2B_2H_6$, in which, it was presumed, the two valency electrons of the metals are absorbed so as to cause the molecule to revert to the ethane-like structure.

At the same time the hydrides are volatile, a property not

generally associated with electrovalent compounds, and in view of a more recent theory it is particularly interesting to notice that to account for this volatility Wiberg (*Berg.*, 1936, **69B**, 2816) supposed that the hydrogen atoms, although linked by electrovalent linkages, were not entirely free, but were bound within the electron shell of the B_2H_4 anion. He suggested that the simplest assumption was an arrangement within the linkage field of the double-bond electrons. To signify this state of affairs he preferred to write the structure as in (XIII), where each positively charged hydrogen ion is associated with one of the negatively charged boron atoms. The structures of the other hydrides were built up in a similar way. That of B_4H_{10} was written as in (XIV), since it can be formed by the interaction of B_2H_5I with sodium, a reaction analogous to the Wurtz reaction for carbon compounds. In so far as the higher members of the series were concerned, consideration was given to Stock's classification into " boranes " of general formula B_nH_{n+4}, which were written

$$\overset{-}{B}H_2\overset{+}{H} : \overset{-}{B}H\overset{+}{H} . \overset{-}{B}H\overset{+}{H} : \overset{-}{B}H_2\overset{+}{H} \qquad \overset{-}{B}H_2\overset{+}{H} : \overset{-}{B}H\overset{+}{:} \;\; \ldots \;\; : \overset{-}{B}\overset{+}{H} : \overset{-}{B}H_2\overset{+}{H}$$

(XIV) (XV)

$$\begin{array}{c} \mathrm{H}\;\mathrm{H} \\ \mathrm{H}\,|\,\mathrm{H}:\ddot{\mathrm{B}}:\ddot{\mathrm{B}}:\mathrm{H} \\ \ddot{\mathrm{H}} \end{array}$$

(XVI)

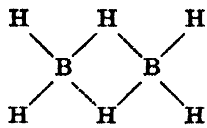
as in (XV), and the " dihydroboranes," of general formula B_nH_{n+6}, which contained $.\overset{-}{B}H\overset{+}{H}:$ groups.

A difficulty arose in respect to these structures, however, when studies of the structure of B_2H_6 by electron diffraction showed that the distance between the two boron atoms is about 1·86 Å., which is greater than the expected single-bond distance and much greater than is consistent with an ordinary double bond (Bauer, *J. Amer. Chem. Soc.*, 1937, **59**, 1096). Shortly afterwards Schlesinger and Burg (*ibid.*, 1938, **60**, 290) obtained evidence that the addition compound of B_2H_6 with ammonia contained one ammonium ion and two BH_3 groups co-ordinated to an amide ion, thus $NH_4[H_3B \leftarrow NH_2 \rightarrow BH_3$. This appeared to support the formulation of diborane as a monobasic acid with one boron atom co-ordinatively saturated and the other unsaturated, as shown in (XVI), a structure which had been suggested in 1923 by Böeseken and in 1925 by Wahl.

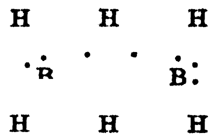
Other early suggestions attempted to express the structures by means of covalent linkages and complete octets, but each introduced

some anomaly which would now be regarded as untenable, although certain of these are of interest in relation to the most recent theories. Thus Ephraim (*Helv. chim. Acta,* 1928, **11**, 1094) suggested that some electrons are shared between three atoms, whilst several suggestions were made involving displacement of the two inner electrons of one or both of the boron atoms in B_2H_6 so as to produce an octet of electrons around each boron atom.

Another distinct viewpoint on these structures is that in which the boron atoms are regarded as having no direct linkage between them, but being linked indirectly through hydrogen bridges (XVII). This structure was first suggested by Dilthey (*Z. angew. Chem.*, 1921, **34**, 596), but he made no suggestion as to the nature of the bridge linkages. A modification of this formulation in which the



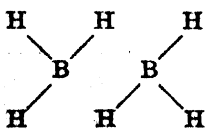
(XVII)



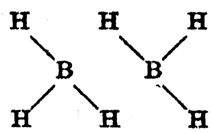
(XVIII)

two bridge hydrogen atoms formed singlet electron linkages to each boron atom (XVIII) was suggested by Core (*Chem. and Ind.*, 1927, **5**, 642), but later it tended to become discarded and almost forgotten. More recent views on resonance, however, have led to its revival.

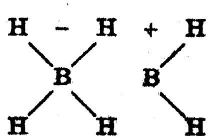
It has been pointed out that the bridge linkage may be regarded as a resonance hydrid, either between the covalent structures (XIX), suggested by Nekrassov (*J. Gen. Chem. Russia,* 1940, **10**, 1021, 1156) or between the ionic structures (XX) which are favoured by Sirkin and Diatkina (*Acta Physicochim. U.R.S.S.*, 1941, **14**, 547).



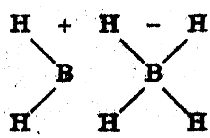
(XIX*a*)



(XIX*b*)



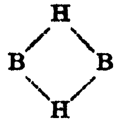
(XX*a*)

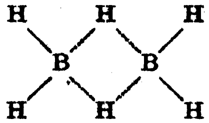


(XX*b*)

This bridge structure has received strong support from Longuet-Higgins and Bell (*J. Chem. Soc.* 1943, 250), who have examined more closely the theoretical implications and practical consequences

of the formulæ. They express the essential linkage in the form (XXI) and hence B_2H_6 is written as in (XXII), with the hydrogen atoms arranged tetrahedrally around the boron atoms.


(XXI)


(XXII)

These structures, containing only paired electrons, are in accord with the diamagnetism of B_2H_6, whilst the absence of a direct linkage between the two boron atoms explains the ease of interconversion of the hydrides and the readiness with which they react with carbon monoxide, ammonia, and amines. It has also been shown by vibrational analysis of this system (Bell and Longuet-Higgins, *Proc. Roy. Soc.*, 1945, **A.183**, 357) that this structure explains the observed infra-red and Raman spectra of B_2H_6. It also explains automatically the resistance to free rotation about the boron–boron linkage which is indicated by specific heat measurements (Stitt, *J. Chem. Phys.*, 1940, **8**, 981 ; 1941, **9**, 780), whilst it has also been pointed out that the products of the electron bombardment of B_2H_6 (B_2^+, B_2H^+, $B_2H_2^+$, and $B_2H_3^+$ particles) are not necessarily inconsistent with the bridge structure.

It is evident also that the hydrogen bridge structure requires the presence of at least two hydrogen atoms, one on each carbon atom. The structure is therefore supported by the fact that whilst mono-, di-, tri-, and tetra-methyl boranes are all known, all attempts to prepare the penta- and hexa-methyl derivatives, $B_2H(CH_3)_5$ and $B_2(CH_3)_6$, have failed. Further, the products of hydrolysis show that neither $B_2H_3(CH_3)_3$ nor $B_2H_2(CH_3)_4$ has more than two methyl groups linked to the same boron atom. This state of affairs was explained, rather unconvincingly, on the singlet electron linkage theory by supposing that such singlet links could exist between boron and hydrogen atoms and between two boron atoms, but not between a boron atom and a carbon atom. Similarly the monomeric $B(CH_3)_3$ is known, but $BH(CH_3)_2$ and BH_2CH_3 appear to dimerise immediately.

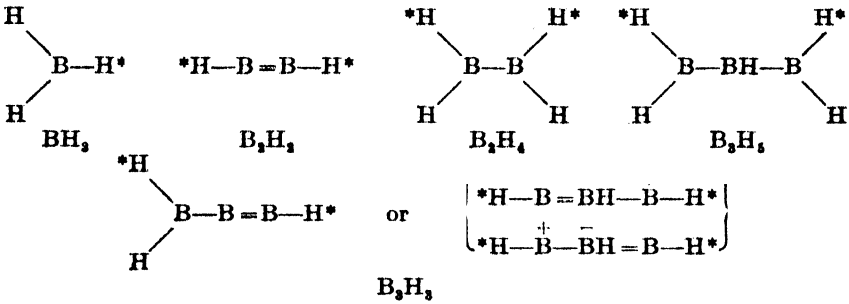
Hydrogen bonds of this type differ essentially from those which occur, for instance, in the association of compounds such as water or ammonia containing OH or NH groups. The latter bonds, formerly attributed to resonance of the type X—H Y, X H—Y are now regarded as depending on the electrostatic attraction between the dipole $\overleftarrow{X—H}$ and an unshared electron pair on the atom Y.

As the B—H linking will have a much smaller dipole moment than the O—H or N—H linkings, and there is no unshared electron pair on the BH_3 group, this form is unlikely to occur in the boron hydrides. Longuet-Higgins and Bell therefore call the bridge linkage in boron hydrides a " resonance link " to distinguish it from the usual hydrogen bond.

It has already been pointed out that one of the strong points of argument in favour of the ethane-like structure, with singlet electron linkages, was the fact that electron-diffraction measurements (Bauer, *J. Amer. Chem. Soc.*, 1937, **59**, 1096) had shown that the boron–boron and boron–hydrogen distances in B_2H_6 are about 1·86 and 1·27 Å., respectively, which are slightly larger than the single-bond distances, this supporting the conception of contributions from single-electron or no-electron linkages. At the same time this was taken as definite evidence of a direct boron–boron linkage, since the closest distance of approach of two unlinked atoms is usually taken as 3·0–3·5 Å. Longuet-Higgins and Bell consider, however, that since in each structure the boron atoms have no unshared electrons in their outer shells, and the electron-density in the lines joining the boron atoms is low, the repulsive force between these two atoms will be much less than in the usual case of unlinked atoms, and therefore they can approach much nearer than the normal distance without any bond being formed between them. Consequently the observed distance of 1·86 Å. between the two boron atoms can be attained without any great expenditure of energy. On the other hand, the high repulsive forces would prevent a similar bridge being formed in cases such as ammonia, water, and hydrogen fluoride, which in consequence must associate only by the ordinary hydrogen bond formation. In fact, similar behaviour could occur only with other hydrides of the general types MH, MH_2, and MH_3 with no unshared electrons in the outer shell. Of these, the alkali and alkaline earth metal hydrides are salt-like in character, so gallium hydride, which has been shown to be dimeric with formula Ga_2H_6, is the only definite example to which this type of structure may be applied, although it is possible that it may exist in the hydrides which are formed by the action of atomic hydrogen on silver, copper, gold, beryllium, indium, and thallium. For the case of aluminium hydride it has been pointed out by Longuet-Higgins (*J. Chem. Soc.*, 1946, 139) that polymerisation may continue until six of the valency orbitals of each aluminium atom are occupied, in which case high molecular weight polymers may be formed in which there are hydrogen bridge linkages from each aluminium atom to three other aluminium atoms. This may account for the fact that it is non-volatile (Stecher and

Wiberg, *Ber.*, 1942, **75**, 2003) in spite of the evidence obtained previously by the same authors (*Angew. Chem.*, 1939, **52**, 372) which favoured a dimeric structure.

To explain the structures of the higher hydrides of boron, Longuet-Higgins and Bell suggest that they are built up from units comprising the BH_3 group and B_2H_2, B_2H_4, B_3H_3, and B_3H_5 groups, the latter all having two hydrogen atoms, indicated by asterisks, to participate in resonance bridges



From these units, it is suggested, the higher hydrides are built up as follows :

B_2H_6 . .	BH_3 ; BH_3	B_4H_{10}	BH_3 ; B_2H_4 ; BH_3
B_5H_9 . .	BH_3 ; B_3H_3 ; BH_3	B_5H_{11}	BH_3 ; B_3H_5 ; BH_3
B_6H_{10} . .	BH_3 ; B_2H_2 ; B_2H_2 ; BH_3	B_6H_{12}	BH_3 ; B_2H_2 ; B_2H_4 ; BH_3

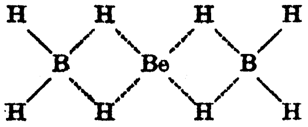
This view, in particular, excludes the possibility of a hydride containing three boron atoms, as is observed.

Beryllium and aluminium both form well-defined volatile mixed hydrides with boron, BeB_2H_8 and AlB_3H_{12}, produced by the interaction of B_2H_6 with $Be(CH_3)_2$ and $Al(CH_3)_3$, respectively (Schlesinger and others, *J. Amer. Chem. Soc.*, 1940, **62**, 3421, 3425, 3429). On the earlier conception of the structure of the boron hydrides these were formulated as the ionic compounds (XXIII) and (XXIV).

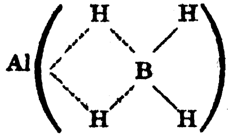
$$Be^{++}(BH_4')_2 \quad \text{(XXIII)} \qquad\qquad Al^{+++}(BH_4')_3 \quad \text{(XXIV)}$$

Such a structure seems quite inappropriate in view of the fact that they are the most volatile compounds of beryllium and aluminium that are known, boiling at 91·3° and 44.5° C., respectively. The alternative theory, assuming resonant covalent structures with singlet electron linkages, implies that boron has a covalency of five, a value not met with elsewhere in the first short period of the Periodic Table. It may be mentioned that the analogous lithium compound, $Li(BH_4)$, is salt-like, of low volatility, and insoluble in benzene, and hence it undoubtedly has an ionic structure.

In terms of the Longuet-Higgins and Bell bridge linkage theory, however, these become of structures (XXV) and (XXVI), respectively,

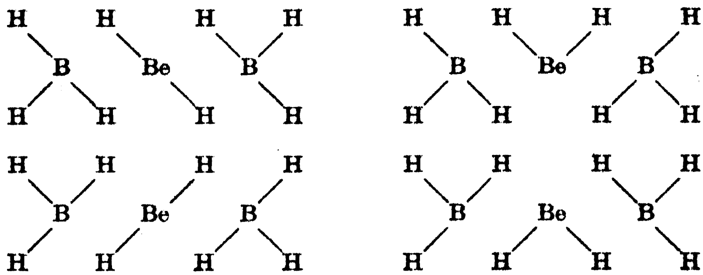


(XXV)

,

(XXVI)

involving resonance forms similar to those of B_2H_6 which in the case of the beryllium compound include



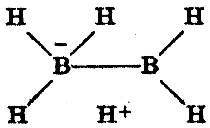
as well as various ionic structures involving BH_4', BeH^+, and BH_2^+.

With such structures the valencies will be arranged tetrahedrally around the beryllium and boron atoms, and octahedrally around the aluminium atom. The prediction that the three boron atoms in AlB_3H_{12} are at the vertices of an equilateral triangle, with the aluminium atom at the centre, is in accord with the results of electron diffraction measurements.

The assumption made by Longuet-Higgins and Bell that the hydrogen atom in a BH_3 group is unlikely to form a hydrogen bond of the essentially electrostatic type with the boron atom of another similar group has been challenged, however, by Buraway (*Nature*, 1945, **155**, 328). He points out that the ability to form such linkages decreases rapidly in the series HF, H_2O, H_3N, H_4C, because the charge on the hydrogen atom being positive will decrease progressively through the first three of these molecules to become negligible or even already negative in methane. In BH_3 it should be more strongly negative, and unlike the completely shielded carbon atom in CH_4 the boron atom, with an incomplete shell, should allow the approach of another hydrogen atom. He also suggests that the increasing charge on the atoms in the series boron, aluminium, gallium, will compensate the lengthening of the interatomic distance and thereby permit the formation of electrostatic linkages in each case. Buraway suggests that this unsymmetrical structure may account for the complex infra-red spectrum of B_2H_6.

Bell and Longuet-Higgins reply by pointing out (*ibid.*, p. 328) that it is unlikely that the $\overset{+}{B}—\overset{-}{H}$ dipole would lead to the formation of a stable dimer without there being any further polymerisation. An indefinite series of polymers would be more probable, as with HF, H_2O and NH_3. If B_2H_6 did contain electrostatic hydrogen bonds the two central hydrogen atoms would not be equidistant from the two boron atoms, whereas the symmetrical structure actually gives good agreement with the infra-red and Raman spectra.

More significant is the theory put forward by Pitzer (*J. Amer. Chem. Soc.*, 1945, **67**, 1126), the main element of which is the conception of a new type of linkage which he calls the "protonated double bond". Referring to the resonance bridge structures, he points out that, at the inter-atomic distances involved, direct bonding between the two boron atoms should also be possible, but that, as indicated by Bauer (*Chem. Rev.*, 1942, **31**, 43) forms such as (XXVII) involve too small a bond angle between the boron–hydrogen and boron–boron linkages. On the other hand, this objection, he



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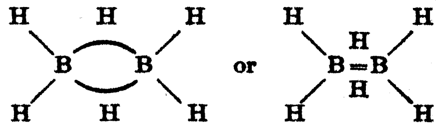


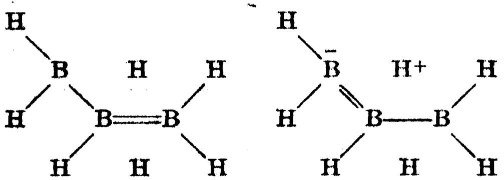
(XXVIII)

suggests, does not apply to a double bond structure (XXVIII) where the electron cloud spreads out in a plane perpendicular to that containing the terminal hydrogen atoms, and the electron density (probability) distribution is therefore not very different from that of a resonance of the forms considered by Longuet-Higgins and Bell, the main difference being a moderate increase in electron density around the protons in the latter. This structure, assuming that the two protons are held within the double bond, recalls the idea put forward by Wiberg.

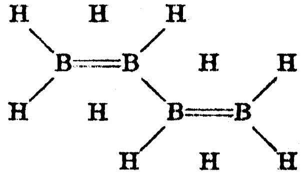
Pitzer considers that this structure is consistent with the observed characteristics of B_2H_6 in that the protons increase the distance between the boron atoms to roughly a single-bond distance, owing to the electrical repulsions, and yet the bond resists twisting like a double bond. Also two additional electrons can be added, the double bond being broken and the two groups to use the new single bonds are already present in the double-bond hydrogen atoms, giving, for example, the $H_3B–BH_3''$ ion; this presence of the protons ready to form separate single bonds make this bond easier to break than a normal double bond. On the other hand, the double-bond protons can be removed by strong bases. Pitzer also suggests

that the electronic energy levels and hence the electronic spectra are very similar to those of ordinary double bonds because protons cannot move appreciably in the time of an electronic transition, but that an excited state stable in a double-bond molecule may cause eventual dissociation of the protonated double bond.

In the higher hydrides Pitzer supposes that the usual conjugation phenomena of double bonds can occur. The interaction of the protonated double bond with an adjacent unsaturated group will give an unstable state in a B_3H_7 (XXIX) but a stable structure will

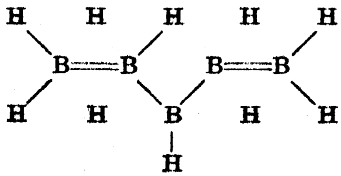


(XXIX)

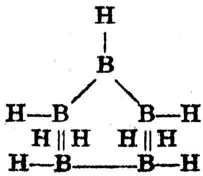


(XXX)

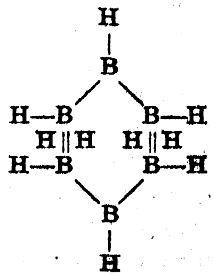
be attained with B_4H_{10} (XXX) and also with B_5H_{11} (XXXI) and B_5H_9 (XXXII). In the latter cases it is suggested that the boron atom with the nominally vacant orbital (incomplete octet), being adjacent to two protonated double bonds, is not only conjugated to both but is also the avenue of interaction between the two double bonds, and therefore it is fully occupied. B_6H_{10} and B_6H_{12} are formulated as six membered ring compounds (XXXIII) and XXXIV) with two and



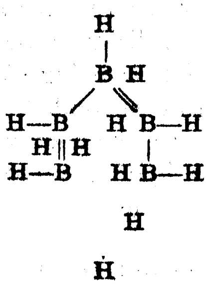
(XXXI)



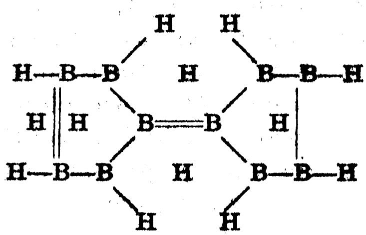
(XXXII)



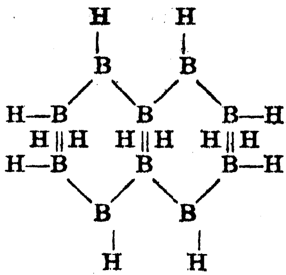
(XXXIII)



(XXXIV)



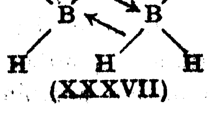
(XXXV)



(XXXVI)

three protonated double bonds, respectively, whilst $B_{10}H_{14}$ can be formulated either with two five-membered rings (XXXV) or with a naphthalene-like structure (XXXVI) as was suggested by Nekrasov (*J. Gen. Chem. U.R.S.S.*, 1940, **10**, 1021, 1156), but the former structure is preferred. In developing these formulæ it was assumed that rings containing less than five boron atoms will be too strained to be stable.

Yet another modification of the bridged linkage formulation has been put forward recently by Walsh (*J. Chem. Soc.*, 1947, 90). This involves an extension of the normal conception of the co-ordinate linkage, in which, when an atom A has an incomplete electronic shell and another atom B has a lone pair of electrons, atom B may donate its electron pair to form a bond between A and B. Walsh points out that there is nothing in the molecular orbital theory to indicate that the donated electrons *must* come from a lone pair, and he suggests the extension of the theory to include the possible donation of bonding electrons as well as of lone-pair electrons. He considers that since, in general, bonding electrons are much more strongly bound than lone-pair electrons, and since a low ionisation potential for the donating electrons is a necessary condition for the formation of a co-ordinate link, the formation of such linkages from bonding electrons will be rare. From the force constant Walsh predicts that the normal boron-hydrogen bonding electrons will have ionisation potentials as low as 10 to 12 volts, however, which are comparable with the ionisation potentials of lone pair electrons (10·8 volts, for instance, in the case of ammonia), and consequently the donation of these electrons becomes possible. On this view, therefore, the structure of diborane may be written as in (XXXVII), where the arrows denote co-ordinate links from the B—H bonds



(XXXVII)

to the adjacent boron atoms. This view recalls the suggestion of Ephraim that electron pairs might be shared by three atoms, and also has some points of similarity to the structures proposed by Buraway and by Pitzer.

Although no definite conclusions can as yet be reached, it is evident that recent theories which are, in point of fact, extensions and amplifications of earlier ideas, are much more closely in accord with the observed properties of the boron hydrides than were the views held eight or ten years ago. Also, as these newer theories are not completely incompatible with one another there seems to be some hope that a more general theory may soon be developed which will cover more than one of these suggestions. It is also, perhaps, not too much to anticipate that such a theory may also be applicable to some other cases where anomalous forms of linkage evidently occur, such as the situation in iron enneacarbonyl, $Fe_2(CO)_9$, and possibly also in the dimeric and polymeric forms of the carbonyls of other metals, where it has had to be assumed that the two metal atoms approach to the usual covalent distance from one another without a direct linkage being formed.

GEOLOGY. By G. W. Tyrrell, A.R.C.Sc., D.Sc., F.R.S.E., The University, Glasgow.

Metamorphism and Metamorphic Rocks.—In N. L. Bowen's paper on "Progressive Metamorphism of Siliceous Limestone and Dolomite" (*Journ. Geol.*, XLVIII, 1940, 225–74) the subject is treated with the aid of a composition tetrahedron, which suggests that the changes may be referred to thirteen steps or grades of increasing decarbonation taking place at successively higher temperatures. In ten of the grades the disappearance of a phase assemblage is accompanied by the appearance of a new phase indicated by a new metamorphic mineral. In most cases this mineral will appear only when the temperature of the appropriate grade is reached. The metamorphic minerals thus become indicators of the grade of metamorphism.

In the order of rising temperature steps the ten minerals produced are tremolite, forsterite, diopside, periclase, wollastonite, monticellite, akermanite, spurrite, merwinite, and larnite. Their natural occurrence suggests that, for the most part, they are produced under conditions which permit their use as temperature indicators.

In three short papers on the cataclastic rocks of the Törne Trask region of Lappland H. A. Brouwer has discussed the origin of *hartschiefer*, those extraordinary parallel-banded rocks which are formed by extreme mylonisation combined with recrystallisation

and metamorphic differentiation ("Über die Bildung von Hartschiefer am Törne Trask (Lappland)," *Geol. Rundsch.*, XXXI, 1940, 154–62; "Über metamorphe Gesteine am Törne Trask (Lappland)," *Proc. Kon. Akad. v. Wetens.*, Amsterdam, XL, 1937, 1–10; "Metamorphic Differentiation in Hartschiefer of Northern Sweden," *ibid.*, XLIII, 1940, 3–9). Rocks of different origins are broken down under these conditions; and by metamorphic diffusion and differentiation during recrystallisation converge to a more or less uniform type of banded rock (hartschiefer). A pronounced alternation of bands and lenticles, which differ in their relative proportions of muscovite and biotite, is developed in the Abisko hartschiefer. This is ascribed to separation of these minerals during an early stage of metamorphism, when biotite was formed along planes of stress relief. Muscovite was formed from feldspar during later stages of rolling-out and recrystallisation.

In a paper on "Mylonization of Hybrid Rocks near Philadelphia, Penn." Miss E. Armstong (*Bull. Geol. Soc. Amer.*, **52**, 1941, 667–94) states that the Pre-Cambrian banded gneiss of this locality is to be interpreted as a hybrid rock, due to the thorough permeation of plagioclase-amphibolite by felsic solutions probably ranging in composition from almost pure water to an aqueous potash-silica-alumina magma. Winding vertical mylonized zones cut these rocks in the western part of the area. These zones enclose lenticular masses of less sheared rocks, and in some places attain a thickness of a quarter of a mile. The mylonite zones are most closely associated with biotite-rich hybrid rocks, and the biotite was formed before the shearing and to some extent guided it. This view is opposed to that of Brouwer (see preceding paragraph).

In describing the "Protoclastic Border of the Colville Batholith (Washington)" A. C. Waters and K. Krauskopf (*Bull. Geol. Soc. Amer.*, **52**, 1941, 1355–1418) state that the batholith is extremely heterogeneous, both structurally and lithologically. A central mass of structureless granodiorite passes outward into a zone of igneous rock with an intricate foliation which is described as "swirled." These swirled gneisses grade into a peripheral belt of variable, well-foliated migmatitic gneisses which, over broad areas, are actually mylonites. That the crushing was protoclastic, and not due to dynamic metamorphism, is proved by the relations of the marginal rocks with the enclosing walls, and by the cementation of the broken fragments with stringers of undeformed quartz and microcline.

F. J. Turner contributes a valuable general discussion of "Current Views on the Origin and Tectonic Significance of Schistosity" (*Trans.*

Roy. Soc. N.Z., **72**, 1942, 119–40), dealing especially with the definitions and nature of schistosity, processes contributing to its development, and the relations of schistosity to the forces and movements of deformation. It is emphasised throughout that schistosity may originate in a number of different ways; and in the interpretation of the different structures the results of the technique of fabric analysis, in conjunction with other structural data, have been found useful by many workers in this field.

Sule Stack, Orkney, the geology of which has been studied by M. Stewart (*Geol. Mag.*, LXXV, 1938, 135–40), consists of a dioritic orthogneiss traversed by shatter-belts and pegmatite veins composed of microcline and quartz. A chemical analysis of the gneiss is given.

A very detailed account of "The Archæan Rocks of the Rodil District, South Harris, Outer Hebrides," has been given by C. F. Davidson (*Trans. Roy. Soc. Edin.*, LXI, Pt. 1, 1943, 71–112). The oldest rocks are paragneisses consisting of forsterite-marbles and calc-silicates derived from original dolomitic sediments, and kyanite-garnet-gneisses from the argillaceous. These sediments were intruded by a complex of anorthosite and banded gabbro or norite. Under the high-grade regional metamorphism which followed eclogites were formed from the basic rocks; garnet-pyroxene-granulites, garnetiferous charnockites, and garnet-bearing anorthositic gneisses from the feldspathic rocks. A phase of migmatisation by quartzo-feldspathic material then followed, by which plagioclase was locally transformed to scapolite and pyroxene to hornblende, and thick masses of acid pegmatites were formed.

At a later stage (Caledonian ?) all the rocks were involved in a zone of intense shearing and dislocation, causing ultra-cataclastic structures and the formation of the low-temperature epidote-saussurite facies.

"The Geology of Ardgour, Argyllshire," described by H. I. Drever (*Trans. Roy. Soc. Edin.*, LX, Pt. 1, 1940, 141–70) is concerned almost entirely with metamorphic rocks. The basement rocks are Moine Gneisses consisting mainly of the normal psammitic and pelitic types, but with an unusual component of limestones. One large basic igneous mass (Glen Scaddle) and several smaller ones have been injected as sheets into the Moines. These intrusions are mainly composed of massive gabbro-dioritic rocks with "appinitic" affinities, and some ultrabasic types. In many places these rocks have been strongly sheared and granulitised. Associated with the larger intrusions are sillimanite-gneisses and various types of hornfels. All these rock-types are fully described and discussed,

with new chemical analyses. There is evidence of contact and regional metamorphism, and of contamination and metasomatism by acid magma.

In a paper entitled "A Petrological Study of the Limestones in the Moine Series of Ardgour, Argyllshire," H. I. Drever (*Geol. Mag.*, **76**, 1939, 501–18) deals with the metamorphic limestones mentioned in the previous paragraph. There are three groups of limestones associated respectively with the granulites and quartzites, with the diorite-gneiss, and with serpentine. The commonest type associated with the Moine sediments is now a basic plagioclase-pyroxene-hornblende-garnet granulite. Limestones associated with diorite-gneiss vary from almost pure marble to calc-silicate and calc-magnesian-silicate hornfels; the mixed types are rich in mica and may contain spinel. Finally there are dolomitic limestones which grade into serpentine. All these rocks have been subjected to high-grade metamorphism, both dynamic and thermal.

In a paper on "Contact Metamorphism by a Tertiary Dyke at Waterfoot, co. Antrim," D. L. Reynolds (*Geol. Mag.*, LXXVII, 1940, 461–9) shows that felsitic material, often spherulitic and resembling truly igneous felsite, has been developed in Triassic pebble-beds at their contact with a dike of olivine-dolerite. Analyses show that this action has resulted from potash metasomatism at a temperature high enough for tridymite to form. The occurrence is paralleled by others in Antrim and Rhum.

D. L. Reynolds has investigated "The Albite-Schists of Antrim and their Petrogenetic Relationship to Caledonian Orogenesis" (*Proc. Roy. Irish Acad.*, XLVIII, Sect. B, No. 3, 1942, 43–66). These rocks are the direct continuation in Northern Ireland of the Dalradian Schists of Cowal (Argyllshire). The albite is sporadic and clearly post-tectonic. The albite-schists have been ascribed to the metamorphism of greywackes and shales (Bailey); to impregnation by soda from outside, at least partially (McCallien)—a view supported by the association of albite with tourmaline; and to metamorphism of a clay rich in detrital albite powder (Bailey and McCallien). (In the writer's opinion there is little difference between the first and third of these theories of origin, for many greywackes and shales associated with them are albite-rich, as they contain much debris of spilitic characters.) Miss Reynolds takes the view that the albite-schists are due to impregnation by soda-rich solutions. After an early introduction of potash into Ben Ledi Schists, solutions of sodium silicate followed, with the concomitant expulsion of potash, iron, magnesia, and possibly alumina. The regional distribution of albite makes it probable that the soda impregnation is related to the

early Caledonian syntectonic igneous activity rather than to the localised post-tectonic phase.

A series of albite-rich rocks interpreted as adinoles occurs between a sill of albite-dolerite and unaltered slates at Dinas Head, Cornwall. They are ascribed by S. O. Agrell (*Min. Mag.*, XXV, 1939, 305–37) to thoroughgoing metasomatism of shales by soda-rich solutions emanating from the albite-dolerite. A volume-for-volume replacement of the slate seems to have taken place, for fine lamination is left undisturbed, large-scale bedding is of the normal type, and fossils occur as perfect casts.

In a later paper Mr. Agrell describes "Dravite-bearing Rocks from Dinas Head, Cornwall" (*ibid.*, XXVI, 1941, 81–93). Dravite is magnesium-rich tourmaline, and is of common occurrence among the adinoles in an extremely fine-grained form as a metasomatic replacement of the original shale. From comparison with other occurrences of dravite it is thought that the source of the boron (or tourmaline) is a conjectural subjacent granite mass. The constant association of albite and dravite suggests a common and contemporaneous origin for boron and sodium. On the other hand, the albite-dolerite contains no boron-bearing minerals. (The writer points out that the late V. M. Goldschmidt's demonstration that boron is highly concentrated as a trace element in Palæozoic marine shales has an obvious bearing on the question of origin.)

In a paper on "Progressive Metamorphism of Sparagmite Rocks of Southern Norway," T. F. W. Barth (*Norsk Geol. Tidsskr.*, **18**, 1938, 54–65) has shown that the unaltered sparagmites of Eo-Cambrian age, and consisting mainly of clastic quartz and microcline cemented by a chloritic substance, grade into schistose rocks, and finally into granulites (Opdal region), with geological continuity demonstrable in the field. The change is accompanied by the introduction of albite. Hence it is believed that the sparagmitic sediments in the zone of Caledonian folding were permeated by soda-rich solutions from which albite was precipitated. (*Cf.* Miss Reynolds's work on the Antrim albite-schists, on page 531.)

"Geological and Petrographical Investigations in the Kongsberg-Bamble Formation" is the title of a new memoir, chiefly on metamorphic rocks, by J. A. W. Bugge (*Norges Geol. Undersök.*, No. 160, 1943, 150 pp.). This Pre-Cambrian formation belongs to the deeper parts of an Archæan mountain range (Sveco-Fennides). It is divisible into an Old Complex, consisting of metamorphic rocks (cordierite- and sillimanite-bearing gneisses and quartzites) and altered igneous rocks of both volcanic and plutonic occurrence, now amphibolites and banded gneisses; and a Younger Complex, migma-

titic in character, consisting of banded gneisses (metataxites), arendalites (a series of norite-charnockite rocks of metasomatic or migmatitic origin), cordierite-anthophyllite rocks, nodular granites containing sillimanite, synkinematic granites, and granite-pegmatites. All these rock types are treated in considerable detail with the aid of numerous chemical analyses.

Another important Norwegian memoir on a metamorphic area is that by I. T. Rosenqvist on "Metamorphism and Metasomatism in the Opdal Area (Sör-Tröndelag, Norway)" (*Norsk Geol. Tidsskr.*, **22**, 1943, 106–202). The area consists of Archæan, Eo-Cambrian, Cambro-Silurian, and Caledonian rocks, in a highly metamorphic condition. The rocks often contain zoisite in equilibrium with acid plagioclase, and it is suggested that a new mineral facies-group is called for—the saussuritic facies. A significant potash metasomatism has taken place, and it is suggested that augen-gneisses and rapakiwi-like rocks should be interpreted as of metasomatic origin, the initial rock material being of basic composition. The mechanism of formation of the porphyroblasts in these rocks is discussed. It is believed that the main metasomatism took place in the late Caledonian after the close of the orogeny.

The first part, "Petrography," of a massive memoir on "Petrologic and Structural Studies in the Bergsdalen Quadrangle, Western Norway," by A. Kvale, has appeared (*Bergens Mus. Aärbok*, 1945, *Natur. Rekke No. 1*, 1946, 201 pp.). This area lies just east of the famous Bergen Arcs. The rocks are divisible into four groups: a basement of typical migmatites consisting of granodiorite-gneiss penetrated by numberless dikes and veins of granite; then a complex of altered quartzites and conglomerates, with a series of altered igneous rocks, originally rhyolites, dacites and diabases with their plutonic equivalents, separated from the basement by persistent strips of mica-schist and regarded as an overthrust mass. The third group consists of Cambro-Ordovician mica-schists associated with an ophiolitic series. The fourth, also regarded as an overthrust mass, is very similar to the second; but the rocks of the lower overthrust mass are in the amphibolite facies, the upper in the epidote-amphibolite facies of metamorphism. The petrography of these varied series is dealt with in great detail with the aid of fourteen chemical analyses.

"Kyanite-Gedrite Parageneses" are discussed by C. E. Tilley (*Geol. Mag.*, LXXVI, 1939, 326–30), especially in relation to a striking example seen by him at Terbeostrov in Russian Karelia. The main rocks of the district are coarse garnet- and kyanite-rich gneisses associated with amphibolites, among which garnet-

amphibolites and garnet-gedritites are common. As shown by analysis the gedrite has a high content of alumina. Aluminium silicate minerals and gedrite (or anthophyllite) have been thought to be antipathetic, and that staurolite and cordierite is the more stable association derived from the same initial material. However, this occurrence (and a few others) shows that this paragenesis is stable under some conditions of metamorphism.

N. E. Odell's memoir on "The Petrography of the Franz Josef Fjord Region, N.E. Greenland, in Relation to its Structure; a Study in Regional Metamorphism" (*Trans. Roy. Soc. Edin.*, LXI, Pt. 1, 1944, 221–46) gives an interpretation of the region which is at variance with that of Backlund and other workers who believe that the phenomena are due to thorough-going Caledonian granitisation (see also, discussion in *Quart. Journ. Geol. Soc.*, CII, Pt. 3, 1946, 443–6). On the contrary, Odell believes that the central zone of granitoid gneisses, amphibolites and paraschists (Basement Series) is Pre-Cambrian, and that the overlying and contiguous sedimentary series (Gregory Series) rests upon it concordantly, no signs of a transgressive relationship being visible. Furthermore, at both eastern and western lateral contacts, the Gregory Series, consisting of micaceous granulites and schists, acquires its condition of maximum stress, and regional metamorphism of the highest grade is developed. On the eastern side of the Basement Series a kyanite-sillimanite zone is found, and on the western kyanite-staurolite schists, with diminishing metamorphic grade farther out. Hence the Basement Series is regarded as an ancient resistant block against which parts of the sedimentary series have been compressed.

In a paper on "Petrology of the Government Reserve Forest, Kodarma, Bihar (India)," N. L. Sharma (*Geol. Mag.*, LXXVII, 1940, 113–40) has described the rocks of a great mica-producing region in India. The oldest rocks are metamorphosed Dharwar sediments now represented by sillimanite- and mica-gneisses and calc-silicate-granulites. These rocks have been injected by a fluorite-bearing granite-gneiss (the Dome Gneiss) which has migmatised the sediments with the formation of oligoclase. The abnormal richness of the country rocks in muscovite is ascribed to pneumatolysis associated with the intrusion of the Dome Gneiss.

B. Rama Rao and T. P. Krishnachar describe "The Cordierite-Hypersthene Granulites and their Associated Schistose Rocks from Bidaloti, Mysore State" (*Rec. Mysore Geol. Dept.*, XXXVI, 1938, 40–75). The rocks probably belong to the Dharwar System. The cordierite-hypersthene granulites are believed to be of sedimentary origin, but have suffered several cycles of metamorphism which

have impressed structural and chemical changes upon them, notably enrichment in magnesia. Basic rocks resembling members of the charnockite series, and described as hornblende- and pyroxene-granulites, are believed to have been derived by plutonic metamorphism from basic igneous rocks and contaminated types injected into the original sediments.

The paper by M. S. Rao on "Geology and Petrography of the Bezwada and Kondapalla Hill Ranges (Kistna District, Madras). Pt. 1. Bezwada Gneiss and Associated Rocks" (*Proc. Indian Acad. Sci.*, XXIV, 1946, 199–215) is the result of field and laboratory study on members of the khondalite group, including gneisses, garnetiferous quartzites, mica-schists, crystalline limestones and calciphyres, which form the country rocks of the region. The khondalites are shown to have originated as argillaceous sediments. They have been intruded by a series of charnockite rocks and by granite. New analyses of garnet-sillimanite-gneiss and of the garnet are given.

The "Amphibolites of the Lead Area, Northern Black Hills, S. Dakota," described by T. A. Dodge (*Bull. Geol. Soc., Amer.*, **53**, 1942, 561–84), are members of a complex Pre-Cambrian terrane, and are found at several horizons emplaced parallel to the structures of the enclosing sedimentary rocks. The evidence supports the conclusion that the amphibolites represent sills of gabbro injected into the sediments towards the close of the dynamic metamorphism, and thus altered by the ensuing movements. A zonal distribution of minerals in the sediments is ascribed to the temperature effect of depth of burial and of igneous intrusion. The amphibolites also were considerably affected by this thermal phase of metamorphism.

In his paper "Some Metamorphic Phenomena produced by Gabbroic Intrusion," C. A. Larney (*Journ. Geol.*, XLVII, 1939, 82–97) describes the metamorphism of the Knife Lake Slates by the Duluth Gabbro, which has led to rocks very similar to the gabbros in composition, but possessing granulitic and granoblastic textures. Several metamorphic zones have been developed, some of which are characterised by abundant orthopyroxene, and thus differ from metamorphic zones developed around granites.

A most unusual metamorphic type is described by C. B. Coetzee in a paper on "Sillimanite-Corundum Rock: a Metamorphosed Bauxite in Namaqualand" (*Trans. Roy. Soc. S. Afr.*, XXVIII, Pt. 3, 1940, 199–205). The rock, which is of Pre-Cambrian age, consists of sillimanite, 70·9 per cent.; corundum, 22·5 per cent.; ilmenite, 6·6 per cent.; and the percentage of Al_2O_3 is 66·3. The rock is believed to have been formed by metamorphism of a highly alumi-

nous sediment, probably a bauxite, under conditions of high temperature and great depth (plutonic metamorphism).

Describing the "Cordierite-Anthophyllite Rocks associated with Spinel-hypersthenites from Toodyay, West Australia," R. T. Prider (*Geol. Mag.*, LXXVII, 1940, 364–82) states that the region is occupied by a varied series of Archæozoic meta-sedimentary and igneous rocks (mostly granite-gneisses). All the data show that the cordierite-anthophyllite assemblage is genetically related to the spinel-olivine-hypersthene-rock, and was derived from it by the addition of silica and by contact metamorphism, both resulting from the intrusion of the granite. The spinel-olivine-hypersthene-rock is believed to have crystallised from a hypersthenite magma which had been contaminated with aluminous material.

In a paper on "Metamorphism of the Jasper Bars of Western Australia," K. R. Miles (*Quart. Journ. Geol. Soc.*, CII, Pt. 2, 1946, 115–55) suggests that these banded ironstones, like those in the Pre-Cambrian of many countries, were originally sedimentary formations which have been subjected to metamorphism, leading to the development of certain characteristic mineral associations. Formerly they were looked upon as silicified and replaced shear-zones in greenstone. With increasing grade of metamorphism the jasper bars have been recrystallised, and the iron in the more ferruginous types has reacted with silica to form minerals such as grunerite, hedenbergite, iron-rich hypersthene and fayalite.

BOTANY. By J. W. G. Lund, M.Sc.,Ph.D., Wray Castle, Ambleside.

Recent Cultural Work on the Lower Algæ in Relation to their Taxonomy and Ecology.—Any attempt to obtain taxonomic or ecological data on micro-organisms by means of cultures is open to the objection that the conditions in the laboratory are too far removed from those in nature. Recently Gerloff (*Arch. Protistenk.*, 1940, **94**, 311), Chu (*J. Ecol.*, 1942, **30**, 284) and Pringsheim (*Pure Cultures of Algæ*, 1946, and *J. Ecol.*, 1946, **33**, 193) have described what appear to be very promising methods for removing such objections. Fritsch, in his introduction to Pringsheim's book, remarks that the polymorphism and bizarre forms of green algæ arising in the cultures of the Geneva school, led by R. Chodat, gave rise to an element of scepticism as regards the value of such cultures (*cf. Scenedesmus*, Chodat, *Rev. Hydrol.*, 1926, **3**, 71). A similar position arose in relation to *Chlamydomonas* after Moewus (*Arch. Protistenk.*, 1933, **80**, 128) produced evidence of marked polymorphism in certain species. Czurda (*Beih. Bot. Zentralbl.*, 1935, **A3**, 196) was unable to

repeat Moewus's results and Gerloff (*loc. cit.*) has made an extensive study of the growth of several species in culture. His results, like Czurda's, show that, in order to define the natural variability of such algæ, healthy, actively growing populations must be studied. Certain features are then found to be constant, while others vary within definable limits. Pringsheim (*J. Ecol.*, 1946, **33**, 193) has developed the soil (or mud) and water (biphasic) cultures, which not only give excellent media for the growth of many algæ but simulate natural conditions. Such algæ can now be studied to determine their natural variability. It will, therefore, be of interest to study various algæ in cultures during the exponential phase of growth. Apart from the desirability of re-examining the polymorphism of such green algæ as *Scenedesmus*, it may be possible to obtain some satisfactory data on desmid variability. Some of the variations described from cultures (*e.g. Xanthidium subhastiferum*, Rosenberg, *New Phytol.*, 1944, **43**, 15) are so great as to suggest that the extreme forms are cultural abnormalities. Such work should go hand in hand with observations on the organisms in nature. It may be that, if an alga is capable of variability such as is seen in culture, then this may be reproduced in nature and be of taxonomic or diagnostic importance. However, conditions in many of the cultural media used are so different from anything known in nature that it may equally be that the forms produced are peculiar to the laboratory. Similar arguments apply to some ecological conclusions drawn from cultural work. For example, though many algæ can grow in the dark in the laboratory when supplied with suitable nutrients (*e.g.* glucose), this is no proof that growth occurs in darkness in nature. Petersen's (*Dansk bot. Ark.*, 1935, **8**, No. 9, 1) experiments show, beyond reasonable doubt, that soil algæ do not multiply to any appreciable extent in the dark under natural conditions, as the laboratory experiments of Bristol Roach (*Ann. Bot., Lond.*, 1926, **40**, 149 ; 1927, **41**, 509 ; 1928, **42**, 317) and others suggested.

Gerloff's (*loc. cit.*) results on *Chlamydomonas* show that the present division of the genus, though of practical value, is not natural, and many species show variability in certain features which bring them into two or more of the present sub-genera, as defined in standard works such as Pascher's *Süsswasserflora Deutschlands, Österreichs und der Schweiz*, Vol. 4. The author (*New Phytol.*, in the press), on much more slender evidence, has come independently to similar conclusions. This is particularly so in chloroplast structure and the related number and position of the pyrenoids. To take one of several examples, the chloroplast of *C. stellata* Dill commonly has a central bridge, in which the pyrenoid lies (sub-genus *Agloë*), but

the lumen between the lower edge of this bridge and the basal portion of the chloroplast may be much reduced (Gerloff, *loc. cit.*, Text-Fig. 24, Figs. 3, 4; Text-Fig. 25, Fig. 8) or lost (Text-Fig. 24, Figs. 6, 7; Text-Fig. 25, Fig. 2). In the latter condition the cells have a cup-shaped chloroplast with a basal (or weakly lateral) pyrenoid (sub-genus *Euchlamydomonas*). Alternatively, there may be two median lateral bulges in the chloroplast, touching, but not fusing to form a central bridge (Text-Fig. 24, Fig. 10). This is a transition to the sub-genus *Chlamydella* (Pascher, *loc. cit.*, Fig. 130, e_3).

Chu (*J. Ecol.*, 1942, **30**, 284; 1943, **31**, 110) successfully cultivated several common plankton algæ, using pure inorganic salts in concentrations (*circa* 0·08–0·15 mg./l. total salts) and combinations that would simulate the different types of natural waters as closely as possible. His results are of great interest. In particular, the fact that, within the optimum concentration ranges of nutrients such as nitrate and phosphate, no increase or decrease in their concentrations or change in the ratio between them can markedly affect the growth of the organisms studied. Some of his comparisons between his cultural results and natural conditions are open to criticism. For example, no growth of *Asterionella* occurred with a phosphate concentration lower than 0·01 mg./l. P; yet in those lakes of the English Lake District to which he refers, and in which *Asterionella* occurs in abundance, concentrations of such an order of magnitude have been found only on one or two very isolated occasions over a number of years, and there is some doubt if the estimates in question were correct. The usual maximum concentration is 0·004–0·005 mg./l. P, and this occurs before large numbers of *Asterionella* are present. Similarly, *Fragilaria crotonensis* is most abundant in these lakes when the concentration of nitrate is below 0·1–0·2 mg./l. N. Yet, in Chu's cultures, no appreciable growth occurred at concentrations below 0·2 mg./l. N. In most cases active growth only occurred at concentrations well above the maximum in the English lakes. It is desirable, therefore, to continue his work. The discrepancy between cultural results and the growth of these organisms in nature may be due to the fact that it is not the concentration of nutrients, between certain limits, which is so important in nature, but the rate of supply of these nutrients, which can be utilised in very low concentrations or against a high concentration gradient. This supply, in nature, is probably governed by the degree of water turbulence.

ZOOLOGY. By William Holmes, M.A., D.Phil., The University, Oxford.

Fossil Fishes.—Fossilised animals form our only record of the course of the evolutionary process; when the record is incomplete all hypotheses of the ancestry of living organisms are based on indirect and conjectural evidence. Recent advances in palæontology have resulted not only from the discovery of new animal remains but even more from the refinement of the methods by which the fossils can be examined, and from the painstaking comparison and connection of one form with another. In recent years the greatest advance has been in our knowledge of the early evolution of the various groups of fishes, amongst which we find the ancestors of all higher Vertebrates, as well as of those of the fish that still survive.

All members of the animal kingdom fall into one of two primary divisions; they are either Invertebrates or Vertebrates. But this dichotomy does not imply an equality of status. The Invertebrates are a heterogeneous assembly; numerically they have a vast preponderance and are far more varied in their form. The latter characteristic is represented by dividing the invertebrate group into a large number of Phyla; the Vertebrates, on the other hand, occupy one Phylum only—the Chordata. Many of the Invertebrates are soft-bodied animals, unlikely to be recorded as fossils, and invertebrate palæontology gives us, therefore, little help in establishing the evolutionary connection between the different Phyla. But the Chordates—that is, the fish, amphibia, reptiles, birds and mammals—have a hard skeleton, often external as well as internal. In consequence our knowledge of the history of this Phylum is now far more complete than it was in the days when the recent evolution of the horse was the only example of an evolutionary series sufficiently concrete to find its way into the text-books.

The most primitive living fish, that is, the fish that are closest to what is believed to be the ancestral chordate form, are two rare animals, *Amphioxus* and *Asymmetron*. These two are the only chordates in which the central nervous system is wholly without that specialisation at the front end that, in all others, forms a brain. The fossil record formerly gave us no indication of the ancestry of these creatures or of their connection with higher forms. But now E. I. White, re-examining an old collection of fossils, has found an animal which appears to lie close to the main stock from which the higher chordates arose, and which is a likely ancestor for *Amphioxus* (*Geol. Mag.*, 1946, **83**, 89). In many features it resembles *Amphioxus*, but differs in having large eyes, and lateral fin folds running the length of the body. It comes from the Silurian

beds of Lanarkshire, and is therefore not as old as some known fossils of higher fish types; in consequence it cannot itself be the chordate ancestor. But its discovery gives us encouragement to hope that we may yet find further evidence on the earliest and most mysterious period of chordate evolution. White has named the animal *Jaymoytius* in memory of J. A. Moy-Thomas, whose book on *Palæozoic Fishes* (Methuen, London, 1939) gives a valuable introduction to this thriving branch of palæontology.

All higher chordates have some sort of brain, and are so called Craniates, in distinction from the *Amphioxus* group, the Acrania. The earliest Craniates, however, are still primitive in that the anterior segments of the head have not yet been modified into jaws; for this reason they are called Agnatha. The inner ear shows an interesting primitive feature in having only two semicircular canals. The only Agnatha living to-day are the lampreys and hagfishes, the surviving representatives of what was once a dominant group. The extinct Agnatha, which failed in competition with the later-evolved jawed fishes, are a group known as Ostracoderms; they first appeared in the Ordovician, and are the only chordates known from these early beds. They flourished in the Silurian and gradually disappeared in the Devonian. They were small animals, seldom more than a foot long, and were covered with a stout external armour of bone.

There are two sorts of skeletal tissue found in Chordate animals: cartilage and bone. The skeleton of the living Agnatha is cartilaginous; so is that of primitive living jawed fish such as the dogfish. Furthermore all those chordates in which the adult skeleton is of bone pass through embryonic stages in which the only skeleton is of cartilage. Is it not therefore reasonable to suppose that cartilage as a skeletal material is older than bone? The discovery of the bony nature of the Ostracoderm skeleton, and other evidence derived from the study of fossil fish, leaves no doubt that, in fact, bone is the older material, and that in the evolution of some chordates it has tended to be reduced and replaced by cartilage. The fact that the internal skeleton of embryos is first formed of cartilage is not a demonstration that development recapitulates evolutionary history; it is merely a special adaptation to embryonic life. Cartilage is the ideal material for the first laying down of a skeleton that must rapidly extend during the growth of the embryo; the manner in which bone is laid down is unsuited to this requirement (Romer, *Amer. Nat.*, 1942, **76**, 394). The cartilage of the lampreys and dogfish is therefore secondary and not a primitive character.

Four main groups (Orders) of Ostracoderm are known; Westoll

has recently raised some important questions in relation to the structure and affinities of one of them, the Cephalaspids (*Trans. Roy. Soc. Edin.*, 1945, **61**, 341). The Cephalaspids were provided with a conspicuous crescentic bony shield over the head region. On either side of the brain this head shield covers cavities which communicate with the brain by canals, and through these it seems that there ran thick nerve trunks. Stensiö, whose work first illuminated this group, suggested that these lateral cavities were occupied by electric organs ; that is, by defensive organs comparable with those found in the living *Torpedo*, the electric ray ; *Gymnotus*, the electric eel ; and *Malapterus*. Such organs generate a powerful electric charge by a modification of the normal process of impulse conduction in nerve or muscle, and they always have, in consequence, an abundant nerve supply. In living fish the electric organ may be of either of two types : usually it is formed from a large mass of modified voluntary muscle ; in *Malapterus* it is said to arise by modification of the tissues of the corium. Westoll believes that the Cephalaspid " electric organ " cannot be of the former type, since the spaces in which it lies are too small to contain the necessary mass of muscle ; it cannot be of the latter type, since it lies internal to the corium. He suggests, as an alternative hypothesis, that these structures, so characteristic of Cephalaspids, were special sense organs, probably responding to vibration in the water, and comparable in function with the lateral line organs universally present in living fish. He points out in support of this view the fact that the lateral line system of Cephalaspids is only slightly developed.

Certain structural features of the Cephalaspid exoskeleton lead Westoll (*op. cit.*) to the conclusion that bone was only deposited within the skeleton when the animal was fully grown. This view has important implications if it is applied to the whole Ostracoderm group. The three other recognised Orders that it contains are the Coelolepids, Pteraspids and Anaspids. The Coelolepids are a poorly known group, and Westoll suggests that one animal long placed within it is, in fact, an unossified Cephalaspid. Other Coelolepids, which show resemblances to Pteraspids, may really be unossified relatives of the latter group. If non-ossification is a larval character there are many interesting possibilities as to the relationships and mode of evolution of Ostracoderms.

The study of fossils not only illuminates the anatomical features of long-dead animals ; it also facilitates speculation on their mode of life and their relations with their contemporaries in other groups. An interesting general study of the Ostracoderms from this point of view has been made by Westoll elsewhere (*Aberdeen Univ. Rev.*,

1942, p. 114). The trunk of a Cephalaspid was more or less triangular in section, and at the lateral angles of the flat ventral side some of these fishes possessed a row of projecting scales. Some also possessed a pair of paddle-like outgrowths from the hind borders of the head shield. These scales and paddles must have served the function of stabilising rudders; do they, therefore, represent the first appearance of paired fins, which are an essential part of the stabilisation mechanism of higher fishes? It appears that, although they are analogous in function they are not, in fact, "ancestral" to paired fins, and that the latter were a new and independent development. This and many other topics are discussed by Romer in a review of 'The Early Evolution of the Fishes' (*Quart. Rev. Biol.*, 1946, **21**, 33).

The next stage in fish evolution is represented by a group known as Placoderms. Watson's study of a large family of these Devonian fishes made it clear that they are an advance on Ostracoderms in possessing jaws, derived by modification from the skeleton of a gill arch; they are still primitive, however, in that the hyoid gill slit, that immediately behind the jaws, has not yet been modified into the spiracle that is characteristic of higher forms. For this reason Watson proposed that the group should be known as Aphetohyoidea (*Phil. Trans. Roy. Soc. B*, 1937, **228**, 49).

Among the Placoderms the Acanthodii have paired fins in varying numbers: some have as many as seven pairs. The chief structural element of these fins is a single spine, and Westoll has traced what seems to be an evolutionary series in the fin structure of the group: in the more primitive forms the spines are almost immobile, broad and short; later members developed special locomotor muscles in relation to the spine, together with extra skeletal elements, giving the fin greater mobility (*Trans. Roy. Soc. Edin.*, 1945, **61**, 381). It is tempting to construct a simple evolutionary series, showing the evolution of paired fins passing from the Ostracoderm condition through that in the Placoderms and leading to the condition in higher fishes. The existence of such a series is implied by Gregory and Raven, who have recently surveyed at length the evolution of paired fins and limbs (*Ann. New York Acad. Sci.*, 1941, **42**, 275). But, as was mentioned above, the evidence seems to indicate that the fins of Ostracoderms were independently developed, and are not ancestral. And, so far as Placoderms are concerned, Westoll takes the view that the paired fins have developed along a "sheaf of phylogenetic lines," and that direct connections between the groups are few. As is so often the case evolution has led animals up a great many "blind alleys," and we must not be too ready to assume that fossils fall into a single progressive line of change. Further

resolution of the problem of the early evolution of the fins requires new knowledge of their internal skeleton, for it is at present fragmentary. But Westoll points out that Gregory and Raven's view is not fully supported by the more substantial evidence provided by the comparison of fossil skulls, which are usually well preserved.

A theory of the first origin of paired fins that has long held the field is the "fin-fold theory." The chief support for this theory came from the study of a fossil shark *Cladoselache*. It was supposed that the primitive fin was a broad fleshy fold in the body wall, supported by a number of parallel skeletal rods; later evolution restricted the fins to a narrower area, and the skeletal elements concentrated to give the fin as we see it to-day. But our more recent knowledge of the spiny fins of Placoderms, animals of greater antiquity than the sharks, shows that the fin-fold theory cannot now be held in its simplest form.

There is no doubt that the paired limbs of land-living chordates evolved by transformation of the paired fins of fish. And, although the fins of living fish are highly specialised structures that could not have been modified in this way, the history of the typical limb of terrestrial forms—the pentadactyl limb—can be traced back through forms of fish now extinct. The story of the evolution of the pentadactyl limb is related by Westoll, who gives his own theory of the manner in which the fin was transformed, and compares and contrasts it with the theories of Gregory and Raven (Westoll, *Proc. Roy. Soc. B*, 1943, **131**, 373).

Moy-Thomas (*Phil. Trans. Roy. Soc. B*, 1940, **230**, 391) has produced convincing evidence that the mysterious little fossil *Palæospondylus*, a fish about 2 inches long, known chiefly from specimens from a mid-Devonian Scottish quarry, is in fact a Placoderm—the only Placoderm without a bony external skeleton.

Towards the end of the Devonian the Placoderms became extinct; some of the last of them to survive fall into a group known as the Stegoselachii. In these animals the characteristic head armour, and the exoskeleton of the thorax, were considerably reduced. By such a process of de-ossification it may be regarded that the next important group of fishes were evolved, for these, the Elasmobranchs, have a cartilaginous skeleton, and never contain true bone. They appeared in the late Devonian and are still represented to-day by the sharks, dogfish, rays and chimæras. In structure they show an advance on the Placoderms in that the first gill slit was probably always modified into a spiracle, and its skeleton played a part in the suspension of the jaw cartilages. Moy-Thomas has surveyed and systematised our knowledge of the

evolution and relationships of this group (*Biol. Rev.*, 1939, **14**, 1). He emphasises that in the earliest times the Elasmobranchs divided up into two groups : the Selachii (sharks, dogfish and rays) and the Bradyodonti (chimæras). The groups are notably distinguished by their tooth structure—a valuable criterion in fossils, for sometimes only teeth survive. The chimæras were always adapted to feeding on molluscs, and so have flattened crushing teeth, while the Selachii have sharp tearing teeth. He was unable to trace any relationship between the Elasmobranchs and any Placoderms, so that this stage in the evolutionary story remains mysterious. But it is quite clear that the Elasmobranchs cannot have been themselves the ancestors of any living non-cartilaginous fishes ; they are a side-line in evolution, and have contributed only the sharks and their relatives to the fauna of the present day.

The bony fishes, which are numerically the masters of the waters of the present time, are known, together with their ancestors, as the Osteicthyes, though, as we have seen, other and earlier forms were also provided with bone. All Osteicthyes have an operculum, which provides a covering to the external apertures of the gill slits, and all have an air-bladder, sometimes used as an additional respiratory organ, sometimes only hydrostatic in function. Both these features are absent from Ostracoderms, Placoderms and Elasmobranchs. The Osteicthyes first appeared in the Middle Devonian, from some ancestor independent of the Elasmobranch line. From the earliest times they separated up into two separate evolutionary lines. One of these lines, the Crossopterygii, contained within it a group known as Osteolepids ; these became extinct in the Permian, but before doing so they gave off an evolutionary line which later led to the amphibia and land-living chordates. The ancestor of all chordates higher than fish was, therefore, an Osteolepid. Westoll (*Biol. Rev.*, 1943, **18**, 78) has surveyed this problem of the origin of higher forms from fish. He concludes that the ancestral type was already differentiated in the earliest Late Devonian from a single narrowly defined Osteolepid type. His review also contains a discussion of one of the most difficult aspects of fish palæontology, that of the elucidation of the homologies of the dermal bones of the skull, and the devising of a consistent nomenclature. During the course of development of fish the osteoblasts that are destined to deposit the material of the dermal bones often commence their activity in the vicinity of the lateral line sense-organs and canals. It has been further maintained that the elements of the lateral line system actually induce this bone formation, and are therefore the " cause " of the formation of the

dermal bones. For this reason many writers have used the position of the lateral line canals, which form impressions in the bone, as indications of homology. A bone which contains a given canal in one animal is homologous with the bone containing that canal in another. Experimental work by Moy-Thomas cast some doubt on this convenient practice (*Nature*, 1941, **147**, 681). He extirpated the lateral line sense organs and canal from the frontal region of the head of trout embryos, before the bones had formed. He found that the development of the frontal bones proceeded normally, in spite of the absence of the lateral line. Nevertheless, Westoll maintains that in the earliest fish the position of the sensory pits and canals is still of great value in elucidating bone homology.

The Dipnoi, or lung-fishes, are few in number and of limited habitat; they retain some Crossopterygian characters, but have in many respects been modified; until recent years they were regarded as the only Crossopterygians that had escaped extinction in the struggle for existence. But in 1939 it was announced that a Crossopterygian of the Cœlacanth group had been captured alive off the east coast of South Africa. This discovery caused great excitement amongst zoologists, for the geological evidence had indicated that the Cœlacanths had become extinct millions of years ago. So far no second specimen of this remarkable fish *Latimeria* has been captured, and the first specimen had been considerably mutilated before it could be examined by experts. But enough remained to allow of an extensive investigation of its structure (J. L. B. Smith, *Trans. Roy. Soc. S. Africa*, 1940, **28**, 1). It seems to have changed little from the Cœlacanth form shown by the Triassic fossils. The mystery of how it has escaped capture so long is partly explained by Smith's suggestion that its normal habitat is at a moderate depth beyond the reach of line fishing, and in rocky bottom conditions where trawl nets cannot operate. Here it probably crawls among the rocks and rarely swims to a higher level.

Of the second and now dominant group of Osteicthyes, the Actinopterygii, little can be said here. They are the descendants of those early forms that "decided" to remain fish while their relatives ventured on to land and became our own ancestors. But mention should be made of a study of a fossil Actinopterygian group, in which Westoll makes many interesting suggestions about the habitat and evolution of these fish (*Bull. Amer. Mus. Nat. Hist.*, 1944, **83**, 1).

NOTES

Calculating Machines (R. E. J.)

Professor D. R. Hartree, F.R.S., discussed recent developments in the design of calculating machines in his inaugural lecture as Plummer Professor of Mathematical Physics in the University of Cambridge (*Calculating Machines*, pp. 40, C.U.P., price 2*s*.). In his undergraduate days, during the first world war, Professor Hartree was a member of a group working at Portsmouth on the problem of anti-aircraft defence. This work involved long numerical calculations and Professor Hartree became interested in the technique of handling numbers. This interest led him last summer to America, where he had the privilege of examining and operating the new calculating machine known as ENIAC, designed by the University of Pennsylvania. His lecture, which deals mainly with the ENIAC, is full of those important details which can be given only by someone who has worked with the machine and fully understood its operation.

ENIAC (Electronic Numerical Integrator and Calculator) was primarily designed for the integration of certain equations connected with ballistics and not specifically as a general purpose machine. It is the first of the new type of calculating machine using electronic circuits as the actual computing elements, and as such paves the way to the future. Its chief limitation when used for general purposes is its comparatively small " high-speed memory," which can only hold up to twenty numbers. Experts now agree that this number should be increased to between one and five thousand. A system of punched cards is provided to supplement this memory, but the use of such a system is cumbersome for calculations involving large numbers of intermediate results and is, of course, much slower in operation.

A most important unit of the ENIAC is the " Master Programmer," which organises the computing sequence and makes the change from one sequence to another. Claims have been made that the machine can judge when to change from one operation to the next, but this judgment is extremely limited. The machine obeys blindly the sequence laid down for it, and in this connection Professor Hartree speaks of the necessity of developing what he terms the " machine's-eye view " of the problem, that is, the ability to foresee what will happen when the machine does just what it is told to do, no more or less. If the work leads to unpredictable results, such as a division by nought, the machine still follows the sequence prescribed for it and the calculation breaks down. Professor

Hartree devoted the latter part of his lecture to a consideration of the effect that this new tool will have on mathematical physics and statistics, and to the problems which can be solved if the ability of a machine, which can make a million multiplications in an hour, is fully appreciated and utilised. It is interesting to notice, in one of the examples given, which deals with the solution of a large number of simultaneous equations, the method which is most suitable for use on the ENIAC. It consists of re-arranging each equation so that its right-hand side is equal to zero, of then squaring and adding the equations and finding the values of the variables which make this necessarily positive sum a minimum. This method, using the quadratic form to solve linear equations, is one example of the necessity of starting "to think the other way round" when using the machine. Similarly the present-day tendency to take the differential equation as the fundamental statement of a physical problem may give way to the use of the integral equation, when the phenomenon as a whole may be examined.

Professor Hartree's lecture gives a comprehensive but still concise account of this new tool. The latter part is illustrated by mathematical examples, which are given in sufficient detail to be followed easily. The lecture leaves the feeling that, with the advent of modern calculating machines, the time has come to reconsider the solution of those problems which were not tackled in the past because of their arithmetical complexity, and to consider carefully the new types of problem which can be tackled with confidence in the future.

Papin's Tercentenary (M. Schofield)

To recall the birth 300 years ago of Denys Papin should strike a resonant note among three sections of pure and applied scientists. The physicist will naturally claim "priority" (to use an over-worked term) in commemorating this native of Blois who was a physicist himself before taking the chair of mathematics at Marburg, who was collaborator of Huygens and Boyle, and a Frenchman elected F.R.S. and "temporary curator of experiments" to that body. How well one remembers the picture of Papin's Digester in early physics textbooks! In particular Everett's English translation of Deschanel's *Traité de Physique*, though now so "old fashioned," found full space for the bronze boiler with burning coals below, a boiler with the first safety valve working on the lever-plus-weight principle—all to demonstrate, as far as the physicist goes, that water may be taken to well over 100° C. within a closed vessel.

But the engineer and the food technologist will have some say in Papin's contributions to knowledge. In the birth of the steam-

engine the digester was an important step in itself, apart from Papin's subsequent conversion of it into a condensing engine. After the threat of religious persecution had driven him to London, Papin described his digester in 1681. He spent some years here, was off again to the Continent, but returned in 1675 for a short spell to outline a second idea which engineering science will claim, *viz.* the pneumatic transmission of power which Papin demonstrated when he exhausted a chamber, connected a pipe to the point where power was needed, and on withdrawing air behind a piston, saw atmospheric pressure move the piston. After moving to Marburg Papin worked on Huygen's gunpowder engine, the first (though impracticable) gas-engine. So it is not surprising to find him thinking now of his digester as an engine boiler; of causing the steam to push up a piston to be caught in a latch, and then on withdrawing the fire below, to cause a partial vacuum and see the return of the piston. Since the piston did work in pulling a rope attached via a pulley to a weight, Papin's "engine" was born as intermediate between Hero's Aeolipile and Watt's steam engine (Watt began with a Papin boiler).

Yet why did Papin construct his "digester," and call it such? There the food technologist scores. For Papin, like Appert and other inspired Frenchmen, had become interested in food preparation. "I took some beef bones that had never been boiled . . . these being put into a little glass pot with water . . . and after the vessels being cooled, I found very good jelly, which, with sugar and juice of lemon, I did eat with as much pleasure as jelly of Hartshorn." That experiment on "digesting" bones proved of greater significance than all Papin's other work on the air-pump, with his two-way tap and his double-barrelled pump; on hydraulics; and on the exhausted bell-jar receiver which demonstrated the part played by air in sound transmission.

Miscellanea

The following were elected to be Fellows of the Royal Society at the meeting held on March 20: Dr. W. J. Arkell, formerly senior research fellow of New College, Oxford; Dr. G. M. Bennett, Government Chemist; W. S. Bisat, civil engineer; Mary Lucy Cartwright, fellow of Girton College and lecturer in mathematics in the University of Cambridge; Prof. E. J. Conway, professor of biochemistry, University College, Dublin; Prof. T. G. Cowling, professor of mathematics in the University College of North Wales, Bangor; J. Craigie, member of the scientific staff of the Imperial Cancer Research Fund, London; M. B. Crane, head of the Pomology

Department of the John Innes Horticultural Institution, London; Prof. W. J. Duncan, professor of aerodynamics at the College of Aeronautics, Cranfield; Prof. M. G. Evans, professor of physical chemistry in the University of Leeds; Dr. W. S. Feldberg, lecturer in physiology, University of Cambridge; T. Goodey, principal research officer, Institute of Agricultural Parasitology, St. Albans; Dorothy C. Hodgkin, fellow and tutor of Somerville College, Oxford, and University demonstrator in chemical crystallography; J. Hutchinson, keeper of the museums, Royal Botanic Gardens, Kew; Dr. D. A. Jackson, lecturer in spectroscopy, University of Oxford; Prof. G. Jefferson, professor of neurosurgery in the University of Manchester; Prof. H. A. Krebs, professor of biochemistry in the University of Sheffield; Dr. F. G. Mann, reader in organic chemistry and fellow of Trinity College, Cambridge; Prof. P. B. Moon, professor of physics in the University of Birmingham; Dr. E. Orowan, Cavendish Laboratory, Cambridge; Prof. F. A. Paneth, professor of chemistry in the University of Durham; Muriel Robertson, head of the Department of Protozoology of the Lister Institute, London; Prof. F. J. M. Stratton, professor of astrophysics in the University of Cambridge; Prof. C. H. Waddington, professor of animal genetics in the University of Edinburgh; Air Commodore F. Whittle, adviser to the Controller of Supplies (Aircraft), Ministry of Supply.

Princess Elizabeth has been elected a Royal Fellow of the Royal Society.

The Holweck Prize for 1947 of the Physical Society and the Médaille Holweck of the Société Française de Physique have been awarded to Prof. E. N. da C. Andrade, Quain professor of physics in the University of London, in recognition of his experimental investigations on the solid and liquid states. Other medals awarded during the quarter include those of the Royal Geographical Society: Founder's Medal to Brigadier Martin Hotine, director of Colonial Surveys, Patron's Medal to Colonel Daniel van der Meulen, and Victoria Medal to Prof. E. G. R. Taylor, emeritus professor of geography in the University of London; the Linnean Medal of the Linnean Society of London to Prof. M. Caullery of the University of Paris; a Valdemar Poulsen Gold Medal of the Academy of Technical Sciences in Copenhagen to Dr. E. F. W. Alexanderson and to Sir Robert Watson-Watt; and the James Watt International Medal of the Institution of Mechanical Engineers to Prof. S. Timoshenko.

Sir John Lennard-Jones, Plummer professor of theoretical chemistry in the University of Cambridge and chief scientific adviser

to the Ministry of Supply, has been appointed chairman of the Advisory Council on Scientific Research and Technical Development, Ministry of Supply, in succession to Sir Frank Heath.

The following appointments have been made to chairmanships of research boards of the Department of Scientific and Industrial Research: Sir Edward Salisbury to be chairman of the Forest Products Research Board in succession to Prof. V. H. Blackman; Engineer Vice-Admiral Sir Harold Brown to be chairman of the Fuel Research Board in succession to Sir Harold Hartley; Sir Stanley Angwin to be chairman of the Radio Research Board in succession to Lieut.-Col. Sir George Lee.

Dr. Franklin Kidd, superintendent of the Low Temperature Research Station, has been appointed director of food investigation, Department of Scientific and Industrial Research, in succession to Dr. C. S. Hanes, who has become head of a unit of biochemistry which is being set up at the University of Cambridge by the Agricultural Research Council. Dr. E. C. Bate-Smith, senior principal scientific officer at the Low Temperature Research Station, has been appointed superintendent of the station.

We have noted with great regret the announcements of the death of the following scientific workers during the past quarter: Sir Joseph Barcroft, F.R.S., emeritus professor of physiology in the University of Cambridge; Mr. W. J. Bean, C.V.O., formerly curator of the Royal Botanic Gardens, Kew; Dr. F. F. Blackman, F.R.S., formerly reader in botany in the University of Cambridge; Prof. L. Cobbet, formerly professor of pathology in the University of Sheffield; Dr. J. D. Falconer, formerly director of the Geological Survey of Nigeria; Prof. V. M. Goldschmidt, For.Mem.R.S., formerly professor of geology and mineralogy in the University of Oslo; Dr. D. Hooper, formerly of the Wellcome Historical Medical Museum; Prof. P. Janet, formerly professor of psychology in the Collège de France; Prof. L. W. Lyde, emeritus professor of geography in the University of London; Sir Halford Mackinder, P.C., sometime director of the London School of Economics and Political Science; Prof. B. A. McSwiney, F.R.S., professor of physiology at St. Thomas's Hospital; Prof. R. Newstead, F.R.S., emeritus professor of entomology in the University of Liverpool; Prof. Ll. G. Owen, formerly professor of mathematics in the University of Rangoon; Prof. W. Ramsden, emeritus professor of biochemistry in the University of Liverpool; Prof. P. M. Roxby, formerly professor of geography in the University of Liverpool; Dr. A. Scott, F.R.S., formerly director of scientific research at the British Museum; Dr. H. M. Tory,

formerly president of the National Research Council of Canada; Dr. W. L. Valentine, editor of *Science* and formerly professor of psychology in Northwestern University; Mr. H. A. S. Wortley, principal of University College, Nottingham.

The Jubilee Memorial Lecture of the Society of Chemical Industry for 1946 was given by Mr. F. P. Dunn and dealt with British Chemical Publications. The greater part of the lecture was concerned with the history of the publications of the Chemical Society, the Royal Institute of Chemistry, the Society of Chemical Industry and the Bureau of Abstracts which is maintained jointly by the two Societies, the Physiological, Biochemical and Anatomical Societies and the Society for Experimental Biology at a cost, in 1945, of £18,666. The lecturer had, however, much to say of wider interest. He gave a clear exposition of the restrictions, imposed by the Government, which cause books published in this country to be less attractive in appearance than those produced in the United States and gave statistics which showed that, before the last war, the number of scientific and technical books published each year in Great Britain was considerably greater than the number published in the U.S.A. He estimated that our printers, still short of staff and without replacements of machinery, will take at least five years to catch up arrears of work so that it is unlikely that the pre-war ratio will be reached for some years.

The Societies are still handicapped by lack of paper. *Chemistry and Industry* is allowed only 64 per cent. of its pre-war consumption and although the *Journal of the Chemical Society*, the *Journal of the Society of Chemical Industry* and the *Abstracts* are allowed 100 per cent. of their pre-war quota the membership of the Societies has nearly doubled. The influx of papers is so great that, on an average, six months elapse from the date of receipt of a paper to the date of its publication.

Speaking of the future of the *Journal of the Society of Chemical Industry* Mr. Dunn regretted that the policy of some of the big chemical organisations should appear to be opposed to the publication of the results of industrial research. The prestige of British chemistry to a large extent depend on the quality of British chemical publications and if the large and important firms attract the best chemists and then refuse to allow their achievements to be made known the reputation of British work will inevitably decline.

The International Committee of Weights and Measures held its first plenary session for nine years in October last. Mr. J. E. Sears

of the National Physical Laboratory was elected president for the session and M. Dehalu (Belgium) secretary. The Committee carried out the usual formal inspection of the vault in the Bureau International des Poids et Mesures in which the International Prototypes of the Metre and Kilogramme are kept, and were able to see that the reinforcement of the vault had preserved the standards from damage from the bombs which fell in the grounds of the Bureau. The International kilogramme has been compared with the working standards employed in the Bureau for the first time since 1889 with results which, after special cleaning of the metal surfaces, agreed in each case, within 0·05 mgm. with those obtained at that time. The working standards of the metre have been re-engraved and with improved methods of observation it is claimed that two of them can be compared within $\pm$ 0·1 micron (*i.e.* $\pm 1 \times 10^{-7}$ metre).

The Committee decided that on and from January 1, 1948, the absolute electrical units based on the M.K.S. or C.G.S. system should take the place of the present units based on the mercury ohm and the silver voltameter and adopted the following conversion factors: 1 international ohm = 1·00049 absolute ohm; 1 international volt = 1·00034 absolute volt. On the same date the present international candle will be replaced by a unit of candle-power of such magnitude that the luminous intensity of a black body at the freezing-point of platinum is 60 c.p. per sq. cm. But for the war all these changed units would have been adopted on January 1, 1940.

The *Bell Laboratories Record* for February 1947 (Vol. XXV, No.2, pp. 70–74) contains an account of an Optical Proximity Fuse which was developed during the recent war. This particular fuse was designed to fit into the nose of a 4½-in. rocket, for use against aircraft.

The great advantage of a proximity fuse is that its moment of detonation is decided by the target itself, *i.e.* the aeroplane. In the older types of fuse which were pre-set, the trajectory of the projectile might have been correct, but due to small errors in the fuse setting the explosion would take place out of range. A 4½-in. rocket, travelling 100 ft. in $\frac{1}{10}$th second, would obviously require an extremely accurate type of pre-set fuse to ensure detonation at the correct point. In addition, the optical proximity fuse can automatically make allowance for certain small changes in the aeroplane's course after the projectile has been fired. Similar types of fuse were developed during the war, using Radar principles.

The fuse operates when the intensity of the light falling on it suddenly changes, as it will do on approach to the target. A toroidal

lens focuses the light on to a small photocell which is connected to a valve amplifier. The output of the amplifier, which is nil until there is a sudden change of light intensity, is made to operate a thyratron discharge tube. This in turn starts the chain which ignites the explosive charge.

The toroidal lens forms part of the conical nose of the rocket and is made of optically clear methyl methacrylate, commercially known as lucite or plexiglass. The lens was made by injection moulding to the final dimensions and no polishing was required after moulding. The lens was designed to transmit only light received from a narrow angle around its circumferential surface, this being achieved by having an opaque covering over part of the lens and also by a suitable choice of curvature. This narrow angle was further defined by a slit opening to the photocell. By these means the fuse is made to "see" the target when the latter is in the densest part of the fragmentation pattern.

The development work on the fuse had two major problems to overcome. Firstly, all the components had to fit into a very limited space and miniaturisation was essential. Secondly, the components had to be capable of withstanding the accelerations, of the order of $1000g$, experienced when the rocket is fired. It was essential to meet these requirements without reducing the size of the explosive charge and also in a form suitable for cheap mass production processes.

To provide a shockproof mounting, the valves, condensers, etc., are mounted individually in holes cut in a wooden block which was then covered in wax. Allowance was made for the variable characteristics of the amplifier valves by matching them with suitable grid bias resistors and condensers before they reached the assembly line. The power supply is a small cylindrical battery unit.

The fuse is provided with safety switches to prevent premature operation if the fuse were accidentally dropped before being fired and the amplifier is also prevented from functioning until the projectile is a good way along its trajectory. An additional self-destruction arrangement is provided to make the projectile explode before reaching the ground, in the event of it missing the target.

To a large extent the success of this type of fuse was due to the recent developments which have been made in the processing of plastics, in die-casting and in impregnating compounds. It is a neat solution to the problem of exploding the projectile at the correct point in space, but it is still a sorry reflection on the state of modern civilisation that such a beautiful mechanism was made solely for purposes of destruction.

O O

REVIEWS

ASTRONOMY

An Introduction to the Study of Eclipsing Variables. By Z. Kopal. Harvard Observatory Monograph No. 6. [Pp. x + 220, with 2 figures.] (Cambridge, Mass.: Harvard University Press; London, Oxford University Press, 1946. 22*s.* 6*d.* net.)

This book is a fairly exhaustive treatise dealing with the theoretical interpretation of the light curves of eclipsing binary stars. Nobody requiring an introduction to the whole subject of eclipsing variables, or even to that aspect of it covered by photometry, should, however, be misled by its title into starting with it. For instance, though practically every page is concerned with the analysis or interpretation of light curves, not one is depicted, and the reader is presumed to be familiar with the many observed types of variation.

This objection to the book's title, however, cannot be matched by any criticism of its contents, once the author's intention is recognised. For research astrophysicists taking up this very complicated field of double-star astronomy, Dr. Kopal's work should quickly become the standard text, collecting as it does all the relevant material hitherto scattered in many periodicals, systematising it and presenting it lucidly and concisely. The flexible graphical methods of the 1920's, based on plausible but oversimplified models of eclipsing systems, are rapidly giving way to more exact numerical methods of successive approximation applied to models that are physically more satisfactory, and which take into account such factors as gravity-darkening and ellipticity and reflection effects. This change of emphasis has been made possible by the greatly increased photometric accuracy afforded by photoelectric apparatus, and it will be accelerated by the systematic and painstaking treatment outlined by Dr. Kopal in this book.

The first half of the memoir deals with geometrical considerations; the eclipses of spherical stars seen as concentrically darkened circular disks, the derivation of orbital elements from the observed light curves, and the improvement of preliminary elements to allow for limb darkening and eccentricity. The second or dynamical half deals with the modifications introduced into the light curves when tidal forces and axial rotation cause the components to depart from sphericity. Here a physical model is first developed to represent a distorted star in equilibrium, the effect of the distortion on the isophotes is then discussed, and the net result on the light curve both inside minima and between eclipses is estimated. The last chapter discusses the various methods for determining and rectifying the elements of close eclipsing systems, and brings the reader right up to the present frontier of research in this field.

He would be ill-advised to engage in the fray, however, without knowing something of the function of his allies in the general plan of attack. Dr. Kopal's book tells only half the story; for the rest, the part covered by radial velocities and spectroscopy generally, there is only the current periodical literature as guide. What we now need is a companion volume to Dr. Kopal's excellent memoir which will, in conjunction with the present book, form a comprehensive treatise really justifying the scope of the title. If this supplementary volume is as well done as Dr. Kopal's, astronomy will indeed be indebted to its author. **A. H.**

Earth, Moon and Planets. By Fred L. Whipple. [Pp. viii + 293, with frontispiece and 140 figures.] (Philadelphia: The Blakiston Co.; London: J. & A. Churchill, Ltd., 1946. 18s. net.)

Telescopes and Accessories. By George Z. Dimitroff and James G. Baker. [Pp. vi + 309, with frontispiece and 146 figures.] (Philadelphia: The Blakiston Co.; London: J. & A. Churchill, Ltd., 1946. 18s. net.)

These two volumes in the series of Harvard Books on Astronomy are reprints of war-time first editions called for by a well-merited popularity. Both are written by members of the staff of the Harvard College Observatory, both are intended for the lay reader with an interest in but no specialised knowledge of astronomy, and both are examples of first-class typography, are printed on excellent paper, and are copiously illustrated in a fashion calculated to excite the envy of readers used to the "authorised economy standards" of the past eight years in Great Britain.

Earth, Moon and Planets is a straightforward descriptive account of the solar system as a whole and of its separate components. It is distinguished from the usual run of such books by containing a particularly full description of the earth's status as an astronomical body and of current ideas concerning its internal structure. The chapters on the moon include a well-reasoned discussion of the origin of lunar craters, and in common with those on the separate planets are illustrated with magnificent photographs, many of them previously unpublished. It is perhaps worth noting that Wildt's theory identifying the clouds on Venus with formaldehyde has been withdrawn by its author since the first edition of this book was published. The great Mars controversy lives once again in these pages, though Dr. Whipple can come but to the inevitable conclusion on the reality and significance of the canals. The last chapter on the origin of the Solar System, written before 1941, will presumably be modified in future editions to include both the observational evidence for non-solar planets and the many recent theories which appear to be giving the non-catastrophic hypothesis a new lease of life.

The field covered by *Telescopes and Accessories* lies much more off the beaten track, and its authors are to be congratulated on producing in the first book of its kind a very readable account of instrumental technique in astronomy, which is neither a compilation of working instructions to the amateur building his own telescope nor a mathematical discussion of the optical principles involved in astronomical telescopes. The rapid advances in this field since the invention of the spectroheliosope, coronagraph and Schmidt camera should make this non-technical account (first published in 1945) a best-seller. The authors have taken a catholic view of their subject, and have included short discussions of such related topics as the photographic process and the physiology of the eye. That their book is up to date is attested by the mention of the Maksutov mirror-lens systems, the electron multiplier tube, the direct-intensity microphotometer, the interference monochromator and the "blooming" process. A particularly valuable feature of the book is in three appendices, which are unique in giving data concerning the largest reflecting telescopes (30-in. aperture and over), the largest refractors (15-in. and over), and (though less completely) the largest Schmidt cameras in the world.

These books are worthy members of a series of which the other volumes

are already gracing the shelves of many professional astronomers as well as of those amateurs and laymen for which the series was originally conceived.

A. H.

Frontiers of Astronomy. By DAVID S. EVANS. Sigma Introduction to Science No. 1. [Pp. 175, with 8 plates and 47 figures.] (London: Sigma Books, Ltd., 1946. 6*s*. net.)

IT is not an easy task to write an account of any branch of modern science which shall at once be simple, accurate and entertaining. Those who are familiar with Dr. Evans's work in scientific journalism and in broadcasting know that he brings to this task not merely enthusiasm but also considerable experience; and they will not be surprised that he has produced easily the best book of its kind on astronomy that has appeared for the past twenty years.

In a disarming preface the author announces his intention of giving "an . . . account in simple terms of the sort of problems with which the ordinary working astronomer is concerned." If for "astronomer" one reads "astrophysicist" there can be no doubt that Dr. Evans succeeds admirably in his task. Nor can one cavil at this limitation in view of the title of the book: for there is no denying that the active fringe of astronomy is astrophysics; and the problems of positional astronomy offer few possibilities to the populariser. As for the reader, those with no mathematics or physics will find the book profitable (if rather hard) going; whilst those with school-leaving mathematics and physics will have no difficulty in bringing themselves with its aid right up to date in the methods and results of modern astronomical technique.

After a short historical introduction Dr. Evans goes on to a description of telescopes and spectrographs; and, after dismissing the solar system in 15 pages, gets down to his real concern, the stars and the sun, discussion of which takes up more than half his book. In these chapters the general reader will find all he can reasonably expect to know about the stars; their chemical and physical constitutions, dimensions, temperatures, luminosities, masses, etc.; and, what is more important, he will learn how it is possible to deduce this wealth of information from the rather limited observational resources at the astronomer's command. In the process he will have touched on atomic theory, the elements of spectroscopy, the Doppler effect, Planck's radiation law, and some aspects of nuclear theory—all dealt with in such an entertaining fashion that he will have absorbed painlessly a great deal of information which will stand him in good stead in other subjects than astronomy.

The remainder of the book deals with the spatial arrangement of stars in our Galaxy and the relation of the Milky Way system to the external galaxies. If the treatment here is a trifle summary, at least the author has warned the reader of the fact in his foreword, and no major topic is left undiscussed. Dr. Evans explicitly disowns any concern with the philosophical implications of cosmology, and his attitude here, as elsewhere, is in refreshing reaction against the mysticism of certain other popularisations of astronomy. His claim to have represented in this book the point of view of the ordinary working astronomer, expressed in suitable language for lay appreciation, is amply borne out by its contents.

The book is copiously illustrated by half-tone plates (some indifferently reproduced), by informative line diagrams and by a number of drawings by Victor Reinganum, which will excite a variety of criticisms, but which the

reviewer finds amusing and not so trivial as might appear at first sight. The typography and layout are excellent and the price moderate. If subsequent volumes in the Sigma Introductions are as well planned and well executed as this one, the series will form a notable addition to the popular literature of science.

A. H.

PHYSICS

La Mécanique ondulatoire des Systèmes de Corpuscules. By LOUIS DE BROGLIE, Membre de l'Institut. [Pp. vi + 223, with 19 figures.] (Paris: Gauthier-Villars, 1939. Frs. 250.–)

THE emphasis in this book is placed on the development of quantum mechanics for application to many body problems. It is not concerned with the details of technique, but with the principles involved. These are discussed with the remarkable clarity which one associates with all books by Louis de Broglie. They are in the best French tradition.

Wave mechanics is introduced via the optical analogy to Hamiltonian dynamics. The first chapter recalls to the reader those aspects of the classical theory which are relevant, and in the following chapter wave mechanics is introduced. In the next three chapters the general application to systems of particles is developed. Of special interest is the chapter on the theory of the centre of gravity in wave mechanics. Another feature of particular interest is the discussion of the formation of Wilson Cloud Chamber tracks in terms of the wave mechanical view of a particle or, rather, wavicle. A discussion of perturbation methods leads on to Chapters VII and VIII, which are concerned with systems of identical particles, in the first instance without spin and then with inclusion of spin. Both of these chapters are excellent and should be read by all students of quantum theory. The book concludes with a chapter giving the essential features of a variety of applications—the homopolar bond, spin multiplicity, nuclear spin, band spectra.

This book can be thoroughly recommended to mathematicians and to physicists, both mathematical and experimental. The combination of clarity of style and logical presentation makes it not only very stimulating to read, but also does not demand of the reader a high technical knowledge of mathematics.

H. S. W. M.

Protons, Neutrons, Neutrinos. Leçons professées au Collège de France. By JACQUES SOLOMON, Dr. ès Sc. [Pp. xiii + 228, with 28 figures.] (Paris: Gauthier-Villars, 1939. Frs. 250.– net.)

THIS work, based on a course of lectures delivered at the Collège de France under the auspices of the Peccot Foundation during the 1937–38 session, discusses the fundamental properties of protons and neutrons and of their interaction.

Chapter I shows how the hypothesis of the neutrino has had to be introduced if the conservation laws are to be retained in the process of beta-disintegration. The theory of beta-disintegration is developed in some detail in Chapter II. In the following chapter the theory of forces between the fundamental nuclear particles is discussed, and the problem of reconciling the magnitude of these forces with the known slow rate of beta-disintegration is raised. Short chapters on the magnetic moments of proton and neutron

and on nuclear isomerism follow, and in Chapters VI and VII the author returns to the discussion of the very large interaction between fundamental nuclear particles.

The book was published in 1939 and the bulk of it apparently written somewhat earlier, so that there is only passing reference to the rôle of the meson in the elucidation of the mechanism of the interaction between nuclear particles and of the evidence for the existence of the meson obtained from cosmic ray experiments.

The advances made in meson theory since 1939 tend to make the book somewhat out of date in this respect, but the reviewer knows of no other work in which the theory of beta-disintegration is set out in such clarity. In fact, the whole work is distinguished by a clarity of exposition which seems to be characteristic of French monographs on atomic physics.

The present work is a worthy memorial to its author, who made the supreme sacrifice when he was executed by the Nazis for his courageous activities in the French Resistance Movement.

E. H. S. B.

Introduction to Electron Optics. The Production, Propagation and Focusing of Electron Beams. By V. E. Cosslett, M.A., M.Sc., Ph.D. [Pp. xii + 272, with 8 plates and 155 figures.] (Oxford: at the Clarendon Press, 1946. 20*s*. net.)

Physicists and engineers were faced with problems of electron dynamics ever since the classical discoveries of J. J. Thomson in 1897. But progress was so much hampered by the somewhat clumsy methods of particle dynamics that in the thirty years before 1927 only one instrument was invented of the class which we now call "electron optical": Aston's Mass Spectrograph. Braun's tube was used in physical laboratories in 1927 in almost the same form in which it was left by Braun in 1895 and by Wiechert in 1899. When in 1926 Hans Busch discovered the lens properties of the "concentrating coil" and drew attention to the almost forgotten Hamiltonian analogy of dynamics and optics, physicists and engineers had at last the new "thinking tool" which they so badly needed, and the way to progress was open. In the next ten years the old Braun tube metamorphosed into the modern cathode ray oscillograph and television tube, the electron microscope was born, and countless other electronic devices were invented or at least radically improved by the application of optical principles. As early as 1934 Brüche and Scherzer wrote the first textbook of electron optics, to be followed by many others.

The new book by Dr. Cosslett, well known as a research worker and as an experienced teacher, differs from its precursors by being the first textbook written primarily for the student, and not for the research physicist or engineer. It fulfils its didactical purpose admirably. The book can be read with profit by any student with a knowledge of the elements of physics and of the calculus, without any previous acquaintance with electronics. It will be somewhat less useful to the specialist, as it does not claim to be more than an introduction, and in many cases stops somewhat short of the present-day frontiers of research. But it would have been futile to attempt more in a book of 272 pages without using condensed or advanced methods which would have put it outside the reach of most students.

The first two-thirds of the book contain an elementary but thorough explanation of the production of free electrons and their dynamics in deflecting

and focusing fields. Graphical, numerical, model and experimental methods of field determination and ray tracing are emphasised at the expense of analytical methods. The last third contains a discussion of electron-optical devices, ranging over the whole field of cathode ray tubes, electron microscopes, diffraction cameras, velocity and mass spectrographs, particle accelerators and electron valves of all types, which can serve of course as a first introduction only. The volume is closed by a short exposition of the Hamiltonian Method, which is exemplary in its conciseness and clarity and makes one wish that the author had made more use of these advanced methods in the rest of his book.

There are a few notable omissions, such as the absence of discussions of intensity and space charge problems, and a few minor mistakes, but none of them is likely to mislead the student seriously. The book is generously illustrated, and is likely to achieve the wide circulation which it deserves.

D. Gabor.

Principles of Radar. By Members of the Staff of the Radar School, Massachusetts Institute of Technology. Second edition. [Pp. 887, with 565 figures.] (New York and London: McGraw-Hill Book Co., Inc., 1946. 25*s.* net.)

This book is undoubtedly a very valuable compendium of information on the most important aspects of radar technique. It is copiously illustrated and contains a fund of practical detail which should be of great assistance to students and workers in this field.

The book is designed as a reference text for use in the training of American Army and Navy personnel. This is reflected in the manner of dealing with much of the subject matter. Practical considerations are specially emphasised and there is a tendency to avoid, where possible, mathematical analysis of a problem, even when the alternative is distinctly more cumbersome and sometimes less precise. As a first approach to the study of radar the book has, nevertheless, great merit, and introduces with admirable clarity the essential ideas exploited for this purpose. Only if the reader looks for a detailed theoretical treatment of the principles involved will he be disappointed.

Having presented a general picture of what radar sets out to do, consideration is given to the systems by which the required results may be achieved. The various circuit components are then examined in considerable detail. Timing devices, indicators, receivers, magnetrons, modulators, triode transmitters, radio-frequency lines, radar antennas and propagation, wave-guides and cavity resonators, transmit-receive devices, synchros and servo-mechanisms, are each dealt with in turn.

For this second edition a number of chapters have been largely re-written and are much improved thereby. In Chapter II, however, there seems to be some confusion between electromotive force and fall of potential, the signs of these quantities being used somewhat arbitrarily. Thus, for a condenser circuit the current is negative when the rate of change of potential across its terminals is positive. This is not made clear in the relationships given, for example, on page 2.31. Only one chapter has a bibliography. The others might usefully have followed this example.

Whatever the limitations of this book in regard to theoretical treatment, there can be no doubt that it meets very adequately a real need among more practical workers. The editors, too, are to be congratulated on having

avoided the production of a disjointed collection of works, which happens not infrequently when, as in this case, a number of different authors have subscribed.

H. M. BARLOW.

Antennæ: An Introduction to their Theory. By J. AHARONI. [Pp. viii + 265, with 149 figures.] (Oxford: at the Clarendon Press, 1946. 25*s*. net.)

EVERY wireless aerial may be thought of from two points of view. In the one we try to relate the nature of the radiated or received field to the current in the wire and to deduce its properties as a radiator; and in the other we try to determine the current and potential variations at the input terminals of the aerial, and to deduce its behaviour as a circuit element. Whichever view interests us we desire to know in detail the magnitudes and distributions of the current and potential along the wire. Most engineers have assumed, with little or no proof, that an aerial behaves like a transmission line with a distributed inductance and capacity per unit length which is constant along the wire, from which it follows that the current would be distributed sinusoidally. From the earliest days of wireless transmission, however, theoretical workers have sought to investigate the matter with full mathematical rigour, and, because the theory is necessarily complicated, their papers have not easily been understood by physicists and engineers. The theoretical methods used can be divided into (*a*) those which consider the field equations with boundary conditions appropriate to the aerial (Abraham), (*b*) those in which the conditions to be satisfied by the aerial current are written down as an integral equation (Hallen, King) and (*c*) those in which transmission-line theory is used with critical care to give a good approximation to the case of an aerial (Shelkunoff).

Mr. Aharoni's book provides an excellent account of these methods and shows how they are related to each other. The book will be most valuable to those physicists and engineers who, although able to follow quite complicated mathematical arguments, are not primarily theoreticians, and it will provide a much-needed addition to their libraries. The author has selected his material admirably for readers of this kind, and it is clear that he has much experience of teaching mathematics to physicists and engineers. He explains very fully and clearly how the underlying physical principles are incorporated in the equations and he then shows, with just the proper choice of detail, how results of value are deduced from these equations. Where his judgment shows up so clearly is that he does not allow himself to become unduly immersed in the purely mathematical manipulations which the physicist finds of little interest. For example, he devotes about ten pages (31–41) to a detailed account of the vector relations in some simple types of wave, but assumes that we know all about such things as Hankel functions and Legendre functions. This is just what is required by the majority of physicists and engineers, who are ready to accept the purely manipulative analysis, but who wish to see how their fundamental ideas are embodied in the original expressions.

The author does not attempt to deal with those numerous other matters of aerial theory which lie outside the range indicated above. In particular he does not deal with micro-wave aerials, and his treatment of the radiation diagrams of aerial arrays, their reciprocal properties, and the properties of travelling wave aerials, is much less detailed than his treatment of "standing

wave" aerials considered as circuit elements. It is largely this restriction to the more difficult and less-well-known aspects of the problem which make the book so valuable. It can be highly recommended to all serious students of aerials.

J. A. RATCLIFFE.

Piezoelectricity. An Introduction to the Theory and Applications of Electromechanical Phenomena in Crystals. By W. G. CADY, Ph.D., Sc.D. [Pp. xxiii + 806, with frontispiece and 168 figures.] (London: McGraw-Hill Publishing Co., Ltd., 1946. 45*s*. net.)

THE additional spur of a struggle for national survival presumably accounts for the many scientific and technical advances which originate with wartime activities. Piezoelectricity provides one example, discovered in 1880 by the brothers Curie, the phenomenon remained more or less a scientific curiosity for nearly forty years until Langevin produced ultrasonic waves in water and detected their reflection from submerged objects.

With the availability of the thermionic valve, development forged ahead, and it would have to be a long list which would include all present-day applications of piezoelectric properties; mention of only a few is enough to indicate their diversity. Piezoelectricity now forms the basis of the most accurate clocks, of which the daily drift has been reduced to less than one part in 10^{10}; its use has improved beyond all comparison the measurement of the depth of the sea bed; it is much involved in modern telecommunications and forms the basis of standard radio-frequency control.

This widespread practical use of piezoelectricity has stimulated correspondingly extensive research and Cady, who has been closely associated with this subject since the Great War period, has now presented this comprehensive treatise, covering the entire field of piezoelectricity and some other closely related branches of crystal physics. There is a limited introduction to crystallography, followed by a consideration of the theory of elasticity as applied to all crystal groups. The transformation relations for the elastic constants, to correspond with the rotated axes of crystal slices cut obliquely to the usual crystallographic axes, should prove useful in view of the prevalence of "oblique cuts."

Naturally a study of all the possible modes of vibrations of crystal cuts is essential and the extent of their number and the possibility of their coupling contributes to both "the complexity of the experiment and the perplexity of the experimenter." Piezoelectricity in particular, and the associated physical properties, *e.g.* elasticity, polarisation, pyroelectricity, etc., are fully considered for all crystals, but naturally, throughout the book, particular stress is laid upon quartz and rochelle salt, because their properties have been so much more fully investigated. The piezo resonator and its equivalent electric circuit and the piezo oscillator all receive very full attention, but only a limited space is devoted to their applications.

Rochelle salt exhibits unusual dielectric properties along one axis, displaying hysteresis within a small temperature range, which includes "room temperatures" and which is limited, borrowing a title from magnetism, by two "Curie points." This naturally excites special interest, and a very extensive account is included of this and other "Seignette" crystals, and of the theories of this ferromagnetic analogous property.

All sections contain results of many practical measurements and a liberal

distribution of references, which are in the main gathered at the end into one general bibliography of both books and periodicals.

The book will appeal as a very useful source of reference to all interested in crystal physics and to those with whose work the applications of piezo-electricity are associated, whilst its production maintains the excellent standard which we have been trained to expect. It is a valuable addition to the International Series.

R. E. G.

X-Rays in Research and Industry. By H. Hirst, Nat. Phil. D., B.Sc. (Eng.), A.M.I.E.E., F.Inst.P. Second edition. [Pp. viii + 124, with 82 figures.] (London: Chapman & Hall, Ltd., 1946. 13*s*. 6*d*. net.)

The book contains the substance of a series of lectures delivered by its author before the Melbourne University Metallurgical Society in 1941. The first edition was published in Australia, and met with sufficient success to warrant the publication of a new edition in this country. After a slight introduction, in which the author deals with the production and properties of X-rays and the structure of crystals in seventeen pages, the book proceeds to give an account of the principal methods employed in X-ray analysis and to discuss examples of the applications of these methods with particular reference to metallurgical problems. The emphasis is on the practical and technical aspects of the subject, and there is a very helpful account of the various devices, mechanical and mathematical, which have been worked out by various authors for facilitating the interpretation of the observed spectra. The beginner will find the completely worked out examples included in the book particularly useful guides to his work.

The final section, in which the author attempts to cover the field of industrial radiography in only twenty-four pages, contains a few useful hints to the uninitiated, but is too brief to serve as more than a preliminary introduction to the subject.

The physicist with a good theoretical background, but no technical experience in the application of X-rays to industrial problems, will find Dr. Hirst a useful guide in the preliminary stages of his work. The information compressed into this small book will certainly not convert him into a fully fledged X-ray analyst, but it will help him over the difficult and puzzling preliminary stages. The well-selected bibliography provided will put him in touch with further sources of information.

J. A. C.

Principles of Technical Electricity. By M. Nelkon, B.Sc., A.K.C. [Pp. viii + 240, with 190 figures.] (London and Glasgow: Blackie & Son, Ltd., 1946. 17*s*. 6*d*. net.)

This book is intended for first-year electrical engineering and radio students. The most successful chapters are undoubtedly those (XIV–XVIII) containing a clear and straightforward treatment of the elements of A.C. theory. The simple mathematics of the main text is supplemented by occasional use of the calculus in additional paragraphs not essential to a student approaching the subject for the first time. The rest of the book follows conventional lines and the treatment is apt to be superficial. The thoughtful student will not be satisfied with Chapter IV (primary cells and accumulator). The connection between E.M.F. and transformation of energy is not made clear; the instructions for the use of the P.O. Box omit several important points; the

section on the D.C. potentiometer could be extended with advantage; the charging of an ebonite rod is ascribed to friction; some formulæ (*e.g.* $C = A/11{\cdot}3d.\ \mu\mu F$) are introduced with mysterious factors which are not explained.

There are some rather sweeping statements, but few actual mistakes (*e.g.* Fig. 12 on page 222 is wrong).

A good feature is the inclusion of helpful worked examples in the text. There are questions at the end of each chapter, with answers, and an adequate index. The illustrations are clear and the book well produced by present standards, but the price is high, which is a pity, since the students for whom it was written would wish to possess the chapters on A.C. theory, at least.

F. A. V.

Analytical Experimental Physics. By HARVEY BRACE LEMON and MICHAEL FERENCE, JR. Second edition. [Pp. xvi + 612, with 584 figures and 66 plates.] (U.S.A.: University of Chicago Press; Great Britain and Ireland; Cambridge University Press, 1946. De Luxe edition, 44*s.*; Trade edition, 33*s.* net.)

THIS is the most luxurious elementary textbook of physics which the reviewer has ever handled. Clearly printed on best-quality paper, with pages nearly 12 in. by 9 in. and with wide margins for notes, well bound and profusely illustrated, the book delights the eye, though tires the hands if held in them. The standard is approximately that of H.S.C., though wider in scope and not so detailed in places. The book could be used with great profit by Intermediate B.Sc., First M.B., University Scholarship candidates and First-Year Degree Students, with appropriate selection where necessary. The text is clear, and the slips and obscurities remarkably few. The main section headings are: Mechanics; Heat; Electricity and Magnetism; Wave Motion, Sound and Light. Within these divisions many subjects are treated, though very briefly in some cases.

The book has been revised carefully for the new edition, and about twenty-four new pages added to make room for more extended treatments of atomic and nuclear physics, high-frequency radio, etc. Not all the additions are in the exciting and fashionable branches of physics; *e.g.* there is new material on hygrometry and the properties of dilute solutions. The whole book is now thoroughly up-to-date—for example, the table of Distribution of Electrons in the Elements extends to Atomic Number 96.

Many of the plates are taken from cinematograph pictures of experiments in progress. Some of them, unfortunately, are not very clear, but the idea is an excellent one. There are scattered throughout the text various queries for students to ponder over, and collections of examples at the end of each chapter. A mathematical appendix deals with such topics as elementary calculus and simple determinants. There is a good index.

What more could a student want? Enough money to buy the book, and a reference library at hand (or good teacher) to find out more about many of the topics treated briefly by Lemon and Ference! F. A. V.

Acoustics for Architects. By E. G. RICHARDSON, B.A., Ph.D., D.Sc. [Pp. 90, with 29 figures.] (London: Edward Arnold & Co., 1946. 5*s.* net.)

THIS unpretentious little book gives a clear and readable account of the fundamental principles of design, based on courses of lectures given to students

of Architecture by the Author. It deals with the problems of reverberation, distribution of intensity and insulation, and contains a chapter on the correction of acoustic defects by the use of microphone and loudspeakers.

It seems unfortunate that, in discussing the importance of adequate loudness, the accepted unit, the phon, is relegated to a footnote and that its relation to the decibel is nowhere indicated. There is an obvious misprint on page 62, where "If *no* sound, etc." should read "If *a* sound, etc.," and on page 63 the sound insulation is stated to be proportional to the weight of the partition per unit area instead of to the logarithm of the weight, as the diagram rightly shows.

A good selection of standard data for coefficients of absorption is given, and the diagrams illustrating the chapter on acoustic insulation are particularly clear and convincing. No attempt is made to deal adequately with the more specialised problems of acoustic design, and indeed this intention is expressly disclaimed by the author in his preface, but as a concise account of principles and a useful collection of practical hints the book is to be warmly recommended.

ALEX. WOOD.

Building and Structural Tables: For Architects, Builders and Engineers. By FREDERICK HYDE BLAKE, B.Sc. (Eng.), M.I.C.E., M.I.Struct.E. [Pp. xii + 239.] (London: Chapman & Hall, Ltd., 1947. 21*s*. net.)

THIS book presents in convenient form the data most frequently required in the design and construction of buildings. The information has been grouped by subjects, namely, Roofs: Walls, Floors and Beams; Floors; Beams; Foundations; Services and Fittings; General Tables (relating to Mensuration, Trigonometrical functions, etc.). There are 194 tables in all, giving useful information relating to weights, etc., of typical roof constructions, data concerning concrete, timber, brick, floor finishes, metals, etc., etc. Table 93 gives an extremely comprehensive list of weights of building materials, which should be very useful to designers. The floor section contains tables giving the safe distributed loads for various spans in the case of solid reinforced concrete slabs, hollow-tile floors and filler joist floors. These tables make it possible (except for complicated designs) for the designer to read off directly the thicknesses of slabs and amounts of steel reinforcement. In this way much time may be saved which would otherwise be spent in making calculations.

Useful design formulæ, bending moment coefficients, etc., are inserted at appropriate places; and extracts from current Building Codes of Practice, reports, by-laws and British Standard Specifications are given. It is evident that the author has spared no pains to make his information as up-to-date and accurate as possible. A notable feature of the book is that information is collected in one volume which normally would have to be searched for in many works of reference, building by-laws, etc.

The book can be recommended as a valuable addition to the books of reference of anyone concerned with the design and construction of buildings.

W. M.

A Course of Reinforced Concrete Design. By THOMAS J. BRAY, M.I.Struct.E., M.Inst.B.E. [Pp. viii and 216, with 76 figures and 25 charts.] (London: Chapman & Hall, Ltd., 1946. 25s. net.)

THE author, who is a past lecturer to Derby Technical College, states in his preface that the book consists of amplified lecture notes. It is presented for use as a text book for students and a reference book for the young structural engineer. A very large field is covered, including principles of design of flat slab construction, culverts, tanks, hoppers, domed slabs, retaining walls, etc. Detailed discussion of each of these subjects is impossible in a work of this size and the author's treatment, therefore, is of necessity brief. For this reason, the book is perhaps more useful to the student who already has a little knowledge of the subject than to the absolute beginner.

A few worked examples are given in the text to illustrate principles of design, but, in common with the majority of books on Reinforced Concrete, no examples are given at the end of the chapters for the exercise of the students' knowledge. The charts at the end of the book are provided to simplify design, and these, together with the formulæ for structures such as hoppers and tanks, should prove valuable for reference purposes.

In general the author bases his treatment and permissible stresses on the Code of Practice for Reinforced Concrete (Building Research Board), in which case some explanation is perhaps desirable for the departure from Code Principles in the treatment of axially loaded columns. The Code permits a stress of 13,500 lb. per sq. in. for the steel, whilst the author gives the more orthodox value of the concrete stress multiplied by the modular ratio.

It appears that an error has been made by the author in his treatment of compression reinforcement for beams. The increased resistance provided by the compression steel area (A) is given in the author's symbols as $Afc(m-1)$. fc is taken as the maximum compressive stress in the concrete, whereas it should have been taken as the stress at the level of the steel. If the author for some reason deliberately used the maximum stress, he should have explained and justified this departure from normal design. Such treatment as this can prove very confusing to the student.

The book, including the many diagrams and charts, is very well produced.

W. M.

CHEMISTRY

General Chemistry. By EUGENE P. SCHOCH, WILLIAM A. FELSING, and GEORGE W. WATT. Second edition. [Pp. xiv + 540, with 150 figures.] (New York and London: McGraw-Hill Publishing Co., Ltd., 1946. 20s. net.)

THIS volume, presenting as it does the course of chemistry given to freshmen students at the University of Texas, will appear somewhat unusual to the majority of readers in this country. This has become even more marked in this second edition, which has been entirely rewritten so as to include brief references to the most modern aspects of the subject. Assuming no previous knowledge of the subject it includes not only a summary of the more elementary aspects of chemistry, but also a brief mention of such subjects as atomic numbers and atomic structure, nuclear chemistry, and colloids. It concludes with four chapters on organic chemistry, which sketch over this subject from the very simplest compounds to carbohydrates, proteins, vitamins, and synthetic organic products. It is clearly evident that this does not

permit the detailed discussion of each subject, and particularly of those of fundamental importance, normally to be found in an elementary textbook, nor does it include the methods of preparation and other facts relating to many of the common compounds generally studied in early stages. The layout of the book, however, is refreshing, and it will be interesting to anyone who desires to obtain a broad outline of the subject, without necessarily obtaining a complete understanding of it, and who is content to seek elsewhere for the more detailed information, even on elementary points, which he may require.

J. W. S.

Inorganic Syntheses. Vol. II. Editor-in-Chief, W. C. FERNELIUS. [Pp. xii + 293, with 25 figures.] (New York and London: McGraw-Hill Book Co., Inc., 1946. 20*s*. net.)

DURING recent times inorganic chemistry has undergone a profound transition. Nowadays all modern developments of physics and chemistry find application in what was at one period essentially a descriptive branch of science. It follows, therefore, that inorganic substances present for the research worker problems of infinite variety and open up new fields of inquiry for their more complete understanding. Furthermore, it is generally recognised that, for the successful teaching of chemistry, theoretical knowledge must rest on a firm foundation of experiment. In the laboratory the student finds in inorganic preparations a wide range of interesting chemical reactions calling for experimental skill of a high order. The need for a publication which would give the research worker and the undergraduate detailed and tested methods for the synthesis of inorganic compounds has long been felt. The appearance of *Inorganic Syntheses*, Vol. I, was widely welcomed and the publication of Vol. II eagerly awaited. The new volume is most attractively produced and can be warmly and unreservedly recommended. In the eight chapters the Editor-in-Chief and his associates have brought together a selection of preparations of unusual interest, including rare earths, co-ordination compounds of chromium and platinum, metal carbonyls and acetylacetonates. A feature of particular value is the general summaries which precede a number of closely related syntheses. The book is arranged in chapters numbered according to the periodic classification, but the Editor-in-Chief points out that, since every chemical compound consists of at least two elements, the inclusion of any synthesis in a given chapter on the basis of the periodic table is somewhat arbitrary. Serious consideration has been given to the question of nomenclature, and in the Appendix to Vol. II there are notes on the system which it has been decided to adopt. An example of the application of the system is that beryllium acetylacetonate becomes *bis* (2, 4-pentanediono) beryllium. A number of admirable diagrams enrich the text of this book, and both contributors and publisher must be congratulated on making available a splendid book which every chemist will wish to possess.

W. WARDLAW.

Metallurgical Materials, Alloys and Manufacturing Processes. By V. N. WOOD, A.M.I.B.F. [Pp. xii + 340, with 287 figures, including 33 plates.] (London: Chapman & Hall, Ltd., 1946. 25*s*. net.)

THE recent inauguration of the Institution of Metallurgists has helped to

emphasise the need for training on a broader basis and with due regard for ancillary sciences. Progressive educational institutions, already alive to this, have been reorganising their metallurgical courses to facilitate, in particular, the study of structures and properties of metals and alloys with the aid of the theories of crystal chemistry and of the physics of solids. Industrial metallurgists, keen to apply recent developments and discoveries, have also to concern themselves with day-to-day problems of operating established processes.

A new book on metallurgy with an omnibus title is therefore bound to arouse some interest. The reader will probably be disappointed to find the writer " refraining as far as possible from including too advanced metallurgical data and theories." A fairly extensive but incomplete account of industrial processes is given, but one feels that an attempt has been made to deal with too much material in too small a space and with too superficial a treatment.

A book designed for metallurgical and engineering students should certainly be reliable as far as fundamental physical metallurgy is concerned. One finds an alloy defined (p. 137) as : " A solution, when the constituents are in the liquid state, and a solid solution when the constituents are solid or frozen " ; this is followed by an example in which the freezing of brine is said to result in " a solid solution of salt and water ! " Solidified lead-antimony eutectic is described (p. 140) as a " solid solution " and one encounters (p. 143) such expressions as " a solid solution *of* austenite " and " a solid solution known as cementite—Fe_3C and containing 6·67 per cent. carbon." Errors more easily corrected are the statement (p. 261) that alpha-beta brasses " contain between 46 and 49 per cent. zinc " and the designation that Fig. 247 (Plate XXV) is a photomicrograph showing an *alpha-beta* structure in cast aluminium bronze. Although the earlier treatment of the theory of alloy constitutional diagrams is brief and vague, in following sections statements like " it is *obvious* from the equilibrium diagram " are often made.

The chapters dealing with manufacturing processes are profusely illustrated with photographs of plant, but there are few cross-references from text to appropriate illustration, and one finds surprisingly little attention given to foundry metallurgy. The volume is well-bound and attractively produced.

C. E. Beynon.

Characterisation of Organic Compounds. By F. Wild, M.A., Ph.D., F.R.I.C. [Pp. viii + 306, with 11 figures.] (Cambridge: At the University Press, 1947. 18*s*. net.)

The importance of the characterisation of organic compounds, both old and new, to undergraduate students and research workers alike, has been overlooked all too frequently in the past and a comprehensive treatment of this subject is long overdue. This book begins with a discussion of the reasons underlying the selection of the most suitable reagent for characterisation purposes, and there follows a brief chapter on the general qualitative examination of organic compounds and the separation of mixtures. The preparation of derivatives of the more important groups of organic compounds, *e.g.* hydrocarbons, halides, hydroxyl-containing compounds, carbonyl compounds, acids, amines, etc., is then discussed. The author has given adequate accounts of most of the methods available (up to the end of 1943), noting their limitations, ample references to original papers are provided, compre-

hensive melting-point tables for a wide variety of derivatives have been drawn up, and a notable feature is the provision of full experimental details for the preparation of all the necessary reagents. Author and subject indexes occupy some 29 pages.

In its general conception and in its scope, and in most respects in its detailed treatment of the subject matter, this work is highly to be commended, but the reviewer feels compelled to make certain criticisms, mainly however with reference to presentation rather than factual content. In connection with the latter the omission of ethylenic (and possibly acetylenic) hydrocarbons from the appropriate chapter is undoubtedly serious, more emphasis should have been given to polyfunctional substances, and notes on regeneration from derivatives would have been useful.

The presence of a multiplicity of errors and inconsistencies, especially in nomenclature, and ill-considered spacing of formulæ and equations throughout, which, although possibly not seriously detrimental to the usefulness of this book, are none the less irritating to the reader, particularly at a time when the presentation of scientific works has in general reached such a high standard. It is regrettable that the author did not apparently seek advice on the subject of nomenclature, or at any rate follow one of the standard systems, and also that he chose to employ the grotesquely unfamiliar abbreviations for references as recommended in the *World List of Scientific Periodicals*.

E. R. H. Jones.

Plastics for Production. By Paul I. Smith. [Pp. xvi + 216, with 13 plates.] (London: Chapman & Hall, Ltd., 1946. 15*s*. net.)

This is the second edition of a book intended for those who are interested in the use of plastics in industry. It makes no attempt to describe the methods of manufacture of the various plastics, and indeed the time has long passed when any one person could claim sufficient knowledge of the industry to cover such ground adequately. Small articles are often made entirely from plastic materials, but more often plastics are used to make components for an assembly which may include metals, wood and other materials of construction. The fundamental property of an industrial plastic is, of course, its capability of being shaped during manufacture, but usually some other property or combination of properties is required, such as cheapness, toughness, high or low softening point, transparency, good colour, resistance to moisture or resistance to various chemical reagents. To guide the manufacturer in the choice of a plastic the author has collected in this volume data for the various materials available to the manufacturer of articles, and the result is a good work of reference, whose value is increased by the author's sober and balanced point of view. There are here no fanciful dreams of a plastic age, but a sensible description of plastic materials, in which their defects and limitations are mentioned as well as their advantages.

The book is not entirely without flaws. Some of the definitions in the glossary are too narrow. For example, under "Casting" there is no mention of film manufacture. "Nitration" and "Acetylation" are not necessarily processes applied to cellulose. "Synthetic Resin" is described as "a synthetic thermosetting resin which becomes hard and infusible after being properly cured by heat and pressure." Apart from its resemblance to the classic definition of an archdeacon, the definition is wrong in limiting the term to the thermosetting resins. It is also somewhat of a shock to read a section

on cellulose esters (p. 19) in which there is no mention of cellulose nitrate plastic. On page 24 a note on the American production of acrylic resins has slipped into the section on polystyrene resins. The glossary might well be revised before a third edition is prepared. On the whole, however, the book is highly recommended and will be useful not only to those who use plastics, but also to those who manufacture them and require a handy book of reference.

F. S.

The Dyeing of Textile Fibres. By R. S. Horsfall, M.Sc., and L. G. Lawrie, A.R.I.C. Second edition. [Pp. x + 438.] (London: Chapman & Hall, Ltd., 1946. 25*s*. net.)

The first edition of this book was published in 1927. Since then there have been remarkable advances in knowledge of the structure and properties of textile fibres, in the production of new and improved rayons, in the development of new dyes and in general understanding of the mechanism of dyeing processes. It is not surprising, therefore, that the authors, in preparing the second edition of the book, should have enlisted the services of fourteen specialists as collaborators. The advantages and disadvantages of this arrangement are at once obvious to the reader. Each chapter has been modernised and each is authoritative, but there are disconcerting differences in style; the different authors seem to have written for different types of reader and their work has not been fully co-ordinated. Chapter III, for example, is a model of clarity, suitable for either student or experienced dyer, but other chapters seem to have been written more for the dyer than the student. The author of Chapter IV, dealing with the dyeing of cotton, mentions the Hussong machine without explanation on p. 100, whereas the author of Chapter IX, dealing with the dyeing of wool, describes the machine in fair detail on p. 256. Similarly, although about one-quarter of the book is devoted to cotton, the formula of cellulose is nowhere given or used, whereas, in Chapter VII, the constitution of wool is freely used in discussing its behaviour in various processes. Nine chapters are without references to original papers, though the deficiency is made good, to some extent, by the bibliography at the end of the book; six chapters contain references, though a standard system has not been adopted, and Peirce's name is always incorrectly spelt. These inconsistencies, and minor errors which hurt, such as the use of "Twaddle" for "Twaddell" on p. 99, must not, however, be overemphasised. Every type of reader will find much of great value in the book, which will, no doubt, come to be accepted as a standard text-book on the dyeing of textile fibres.

J. B. Speakman.

An Introduction to Agricultural Chemistry. By N. M. Comber, D.Sc., A.R.C.S., F.R.I.C., H. T. Jones, M.Sc., A.R.I.C., and J. S. Willcox, B.Sc., A.R.I.C. [Pp. viii + 315, with 24 figures.] (London: Edward Arnold & Co., 1947. 8*s*. 6*d*. net.)

The appearance of a textbook on any branch of agricultural chemistry is somewhat of an event, since so few have been written on this important side of food production. The present volume is, therefore, a welcome addition to the library of agricultural science textbooks. It is intended primarily for "students reading for degrees and diplomas in agriculture," and in this respect the authors have succeeded in producing a useful book.

It is divided into three parts, the first of which, entitled "Soil," is really Professor Comber's book *An Introduction to the Scientific Study of the Soil*, rewritten in an abridged and slightly modified form. In a readable and simple manner are set out the chief properties of soil and the main chemical, physical and biological processes which occur in a soil, and attention is drawn to the importance of properly conducted field and pot experiments. A brief account is also given of the formation and classification of soils. The second part is devoted to the principles of manuring and to the properties of the common organic manures and artificial fertilisers. It is regrettable that this section should have been dealt with rather summarily and with few tables or examples of actual fertiliser trials to supplement the text. In the third and largest part, "Animal Nutrition," a good knowledge of biochemistry is assumed, especially as regards structural formulæ, in the chemistry of proteins, carbohydrates and vitamins. Metabolism is treated as fully as might be expected in a textbook on animal physiology, and would appear to be more advanced than is normally required for agricultural chemistry students. Included in this section is a short chapter on dairy chemistry. This is not an unimportant part of a course on agricultural chemistry, and it is therefore surprising to find no mention of the factors causing variations in the composition of milk, the use of the freezing-point depression and the Hortvet cryoscope, or the legal limits for the fat and solids-not-fat contents of milk.

The authors state that a chapter on insecticides and fungicides was prepared, but was not included since it might soon be out of date. There is, therefore, no mention of the chemistry of sprays, dusts, dips, weed-killers, fumigants, soil sterilisers, detergents or water, all of which usually come under the heading of "agricultural chemistry."

There are some differences in style, and in the methods of presenting formulæ and equations, in the three sections, which give the impression that publication may perhaps have been hurried. Nevertheless, this book will be a great help to diploma students, and in later editions possibly sufficient space may be found to deal adequately with the chemistry of milk, insecticides, fungicides, and such other common materials as are used in agriculture.

A. W. M.

The Nation's Food: A Survey of Scientific Data. Edited for the Society of Chemical Industry (Food Group) by A. L. BACHARACH, M.A., F.R.I.C., and T. RENDLE, F.R.I.C. [Pp. xviii + 349, with 4 plates and 12 figures.] (London: Society of Chemical Industry, 1946. 18*s*. net.)

ANYONE unfamiliar with the papers which are the basis of this book would be surprised how absorbingly interesting it is. The volume opens up quite a new world of interesting, and most important, questions, many of which are aptly posed in a stimulating introduction penned by the late Sir Joseph Barcroft, Chairman of the Food Investigation Board. And when all is read, marked, learned and inwardly digested, as Sir Joseph quotes from a shrewd observation of Sir Jack Drummond about the onion: "I cannot but think that there are still things to be found out."

Of course everyone is interested, at least in a mild way, in food. This book is intended not only for the specialist, but also for those with a wider interest in problems of feeding for optimum health. If you want to know about vitamins or trace elements, how foods are processed and preserved, what are

relative nutritive values, what are dietary deficiencies and what they mean to the nation, here is the chance to learn about them in a pleasant and readable volume. And it will set you thinking.

What does the book contain and why does it appear in this form ? The Food Group is a vigorous subject section of the Society of Chemical Industry. It studies food in all its branches and has actively developed the subject for about fifteen years. During the war the Group promoted a series of scientific meetings, at which distinguished investigators contributed papers on the Egg, on Potatoes, on Vegetables, on Cereals, on Meat, on Fish and on Milk as foods. There are twenty-seven original papers by some thirty authors ; these have now been brought together and woven into an authoritative whole by the skilful editing of Messrs. Bacharach and Rendle. In the result they present a balanced diet. And it is true to say that the thoroughness with which the various matters have been surveyed and the literature noted makes it quite certain that all future writings on these subjects will start from where these chapters leave off. They summarise and epitomise our knowledge to date. There are complete bibliographies and an adequate index.

Attention should be drawn to the breadth of treatment. Here is no mere collection of analytical data or arid survey of technological facts, but there is wealth of broad knowledge of the biology of plants, and of animal husbandry and agriculture, in their bearing on the feeding and health of the nation and of the world. Here you may get pregnant suggestions on the effects of sunlight on the plankton of the sea, as well as on the formation and mode of action of vitamins. Yet withal there are still unanswered questions such as why a potato turns black after boiling, and why onions are so nutritious, and the virtues of brown and white bread.

Without doubt the Food Group and the Society have done a real public service in producing this survey. It is of lasting value, and all who have any scientific interest in food, whether production or treatment, will need to possess a copy. It does credit to its authors and editors and will give pleasure to its readers.

H. E. Cox.

BIOLOGY AND MEDICINE

Animal Biology. By Robert H. Wolcott. Third edition. [Pp. xviii + 719, with 508 figures.] (New York and London : McGraw-Hill Book Co., Inc., 1946. 20*s*. net.)

This third edition of the late Professor Wolcott's book has been considerably altered by the rewriting of certain chapters and the addition of others, but it retains essentially its original form—a class textbook and not a work of reference : emphasis has been placed " upon the broader aspects of the science and the general significance of the data presented." Because of this the author has achieved a fresh introduction to his subject, entirely different in scope from the more formal treatment of the usual textbook of Intermediate standard. Possibly he has, at times, cast his net rather too widely, as, for example, in introducing the Ctenophores, Chætognaths and Brachiopods ; it may be questioned whether a somewhat fuller treatment over a slightly less extensive field would not have been preferable—but this is a matter of opinion.

The book is well written and free from errors ; a rather more up-to-date treatment of mitosis than one which involves a spireme might have been

expected, and the statement that "The natural habitats of gorillas are the mountainous forests of Africa" is sufficiently loose to be misleading. The numerous illustrations have been carefully selected and are well reproduced. Save for those who require a more detailed introduction as a prelude to advanced studies, the book serves as a useful and attractive guide to the elements of zoology.

F. W. J.

An Introduction to Social Biology. By ALAN DALE, B.Sc. [Pp. viii + 396, with 189 figures.] (London: William Heinemann, Medical Books, Ltd., 1946. 15s. net.)

THE appearance of a book bearing this particular title evoked great interest amongst the many who are now required to bridge the gap between the General Biology of the first year of medicine and the Special Biology of Man, which is the subject matter of the later years of the medical curriculum. It was interesting, therefore, to learn what in the author's considered opinion is the content of social biology. The author, leading off with a brief discussion of life in space and time, surveys the evidence which permits us to know that modern man is the outcome of a long evolutionary process as yet unfinished. Next he considers man as a mammal, paying attention to the rôle of the endocrines in the maintenance of normality and the production of defect and derangement. He deals also in brief outline with the elements of comparative psychology. Next the biology of sex is dealt with as a comparative study, and the elements of genetics, with special reference to human genetics, are presented. Then comes a discussion on reproduction. The allergies are examined, the typical pathogens described and a number of diseases of social importance considered. The present organisation of the medical service of this country is criticised and a brief historical survey of medicine offered, due tribute being paid to the great names. Then follows a chapter dealing with human needs in respect of food and drink, with special reference to the vitamins and the effects of their insufficiencies. Concluding chapters discuss the balance of nature, social life amongst animals, an account of man's uniqueness and an essay upon the nature of life itself.

The book is admirably produced and bounteously illustrated. Its origin was a series of discussions held with the combined sixth forms (Arts, Science and Modern) of a large boys' secondary school. It is to be judged, therefore, according to its value as a text for such general courses in schools and cultural courses in adult education. It is, as its author says, necessarily experimental in its design. Many of its readers, and particularly those who were looking for a book of this kind for recommending to medical students, will be inclined to regard the author's approach as altogether too traditional. From their point of view it deals far too much with comparative zoology and too little with human and social biology. It remains to be seen whether this book will satisfy the needs of those to whom it is particularly addressed. Did the entrant to the medical curriculum know and understand all that is herein written, then indeed the task of the University teacher would be greatly advantaged. This knowledge and this comprehension could then form the foundation for a course of instruction in social biology as this term is understood by the medical sociologist.

F. A. E. C.

Science versus Cancer. By I. Berenblum, M.D., M.Sc. [Pp. 116, with 8 plates.] (London: Sigma Books, Ltd., 1946. 6s. net.)

While cancer from its nature has understandably attracted a good deal of public interest, there have been few or no authoritative sources to which one could direct the inquiring layman in search of a simple account of the main features of the disease, or of progress in its study. This need has now been admirably met by the present volume, No. 2 in the new "Sigma" series of *Introductions to Science.* Dr. Berenblum presents, in remarkably clear style, good descriptions of such topics as the uniqueness of cancer amongst diseases in general, its wide zoological distribution, and the influence of heredity upon its manifestation. On the last point, it is made evident that there is no single hereditary factor for cancer as a whole, and that the hereditary influences which can be studied by genetical experiment in animals are so slight in their effects as far as man is concerned that they can be largely discounted in practice. On the question of recorded increases in the incidence of the disease, the author is of opinion that these are largely due (excepting probably in the case of cancer of the lung) to changes in age distribution of the population and improvements in diagnosis. Reliable as a source of accurate information, the work is equally useful in correcting common misconceptions, as that cancer is an increasing disease of civilised man: this statement is demonstrated to be untrue for three reasons, *viz.* that the disease as a whole is not confined to man, is not due to civilisation, and is not becoming more frequent in the sense implied.

The vital question as to how best the layman can co-operate in the task of treatment and prevention, without himself becoming morbidly introspective in the process, is answered by showing how he should adopt a rational attitude that neither underestimates the potential seriousness of cancer nor overestimates its frequency, by a real understanding of the prospects and basis of cure in early diagnosis. The whole book is directed to this end, and is materially strengthened by two chapters devoted to the methods and achievements of cancer research, and by plates illustrating the elementary features of cell division, the salient characteristics of benign and malignant tumours, the appearances of occupational cancer of the skin, and the anatomical principles involved in therapy. There is no doubt that Dr. Berenblum, who is an outstanding worker in this field of his choice, has judged it well to spend a part of his time in making available this simple yet balanced and useful account. If in one or two statements (*e.g.* "the fact that cancer tends to arise late in life has nothing to do with the process of ageing") he invites some difference of opinion, his book is free from real errors of substance, and can be warmly recommended not merely to the lay public for which it was written, but to scientific readers as well.

A. H.

BOOKS RECEIVED

(Publishers are requested to notify prices.)

Introduction to Mathematical Statistics. By Paul G. Hoel, Associate Professor of Mathematics, University of California at Los Angeles. Wiley Mathematical Statistics Series. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd., 1947. (Pp. x + 258, with 35 figures and 23 tables.) 21*s*. net.

The Theory of Functions of Real Variables. By Lawrence M. Graves, Professor of Mathematics, University of Chicago. New York and London: McGraw-Hill Book Company, Inc., 1946. (Pp. x + 300, with 12 figures.) 20*s*. net.

Applied Mathematics for Engineers and Physicists. By Louis A. Pipes, Ph.D., Research and Electronics Division, Hughes Aircraft Company. New York and London: McGraw-Hill Book Co., Inc., 1946. (Pp. xiv + 618, with 187 figures.) 27*s*. 6*d*. net.

Atoms, Stars and Nebulæ. By Leo Goldberg, McMath-Hulbert Observatory of the University of Michigan, and Lawrence H. Aller, Indiana University. The Harvard Books on Astronomy. U.S.A.: The Blakiston Co.; London: J. & A. Churchill, Ltd., 1946. (Pp. vi + 323, with frontispiece, 150 figures and 16 tables.) 18*s*. net.

College Technical Physics. By Robert L. Weber, Marsh W. White, and Kenneth V. Manning, Pennsylvania State College. New York and London: McGraw-Hill Book Co., Inc., 1947. (Pp. x + 761, with frontispiece, 50 portrait drawings and 428 figures.) 22*s*. 6*d*. net.

Atomic Energy in Cosmic and Human Life. Fifty Years of Radioactivity. By George Gamow, Associate Professor of Theoretical Physics at the George Washington University, Washington, D.C. U.S.A.: The Macmillan Company; Cambridge, England: at the University Press, 1947. (Pp. xii + 161, with 5 plates and 46 figures.) 7*s*. 6*d*. net.

Die Geschichte der Atombombe. Von Hans Thirring. In the Series "Wissenschaft für Jedermann". Vienna: "Neues Österreich" Zeitungs- und Verlagsgesellschaft m.b.h., 1946. (Pp. 150, with 17 figures and 14 tables.)

Introduction to Atomic Physics. By S. Tolansky, Ph.D., F.I.C., Lecturer in Physics, Manchester University. Second edition, reprinted with Appendix on Nuclear Fission and Atomic Energy. London, New York, Toronto: Longmans, Green & Co., 1946. (Pp. xii + 351, with 5 plates and 115 figures.) 15*s*. net.

Physical Science in Art and Industry. By E. G. Richardson, B.A., Ph.D., D.Sc. Second edition. London: The English Universities Press, Ltd., 1946. (Pp. xii + 299, with 77 figures, including 7 plates.) 15*s*. net.

Sub-station Practice. By T. H. Carr, M.Inst.C.E., M.I.Mech.E., M.I.E.E. London: Chapman & Hall, Ltd., 1947. (Pp. viii + 396, with 287 figures and 27 tables.) 32*s*. net.

Building and Structural Tables for Architects, Builders and Engineers. By Frederick Hyde Blake, B.Sc. (Eng.), M.I.C.E., M.I.Struct.E. London: Chapman & Hall, Ltd., 1947. (Pp. xii + 239.) 21*s*. net.

Aircraft Strength of Materials. By H. D. Conway, M.A., Ph.D. London: Chapman & Hall, Ltd., 1947. (Pp. viii + 256, with 154 figures.) 21*s*. net.

The Escalator Method in Engineering Vibration Problems. By Joseph Morris, Consultant, Structural and Mechanical Engineering Department, Royal Aircraft Establishment, Farnborough. London: Chapman & Hall, Ltd., 1947. (Pp. xvi + 270, with 64 figures.) 21*s.* net.

The Intelligent Use of the Microscope. By C. W. Olliver, A.M.I.E.E., F.R.M.S., Member of the British Mycological Society, Member of the Association for Scientific Photography. London: Chapman & Hall, Ltd., 1947. (Pp. viii + 182, with 53 figures.) 12*s.* 6*d.* net.

Chemistry for our Times. By Elbert Cook Weaver, M.A., Instructor, Phillips Academy, Andover, Massachusetts, and Laurence Standley Foster, Ph.D., formerly Assistant Professor of Chemistry, Brown University. New York and London: McGraw-Hill Book Co., Inc., 1947. (Pp. xii + 738, with frontispiece and 412 figures.) 12*s.* 6*d.* net.

Lecture Experiments in Chemistry. By G. Fowles, M.Sc., A.R.I.C., F.C.S. Third edition, with supplement. London: G. Bell & Sons, Ltd., 1947. (Pp. xvi + 612, with 158 figures.) 25*s.* net.

Advances in Carbohydrate Chemistry. Vol. 2. Edited by W. W. Pigman, Institute of Paper Chemistry, Appleton, Wisconsin, and M. L. Wolfrom, The Ohio State University, Columbus, Associate Editor for the British Isles, Stanley Peat, The University, Birmingham. New York: Academic Press, Inc., 1946. (Pp. xiv + 321, with frontispiece, 17 figures and 14 tables.) 36*s.* 6*d.* net.

The Methods of Cellulose Chemistry. By Charles Doree, M.A., D.Sc., F.R.I.C., late Head of the Department of Chemistry, Chelsea Polytechnic, London. Second edition. London: Chapman & Hall, Ltd., 1947. (Pp. xii + 543, with 81 figures.) 42*s.* net.

Fundamentals of Plastics. Edited by Henry M. Richardson, B.S., Consulting Engineer, DeBell & Richardson, Springfield, Mass., and J. Watson Wilson, Ph.D., Director of Instruction, ESMWT Program, Yale University. New York and London: McGraw-Hill Book Co., Inc., 1946. (Pp. viii + 483, with 199 figures and 60 tables.) 25*s.* net.

An Introduction to Agricultural Chemistry. By Norman M. Comber, D.Sc., A.R.C.S., F.R.I.C., Professor of Agricultural Chemistry, H. Trefor Jones, M.Sc., A.R.I.C., Advisory Chemist and Lecturer in Agricultural Chemistry, and J. S. Willcox, B.Sc., A.R.I.C., Senior Lecturer in Agricultural Chemistry, University of Leeds. London: Edward Arnold & Co., 1947. (Pp. viii + 315, with 24 figures and 27 tables.) 8*s.* 6*d.* net.

Concise Chemical and Technical Dictionary. Edited by H. Bennett, Technical Director, Glyco Products Co., Inc. Brooklyn: Chemical Publishing Co., Inc., 1947. (Pp. xl + 1055.) $10.00.

The Pulse of the Earth. By J. H. F. Umbgrove, D.Sc. (Leyden), Professor of Geology at Delft, Holland. Second edition. The Hague: Martinus Nijhoff, 1947. (Pp. xxii + 358, with 204 figures, 8 plates and 2 tables.) Gld. 20.-.

Peat Moss Deposits in Canada. By Harald A. Leverin. Canada: Department of Mines and Resources, Mines and Geology Branch, Bureau of Mines, 1946. (Pp. vi + 102, with 9 plates and 10 figures.) 25 cents.

Patterns of Mammalian Reproduction. By S. A. Asdell, M.A., Ph.D., Professor of Animal Physiology, New York State College of Agriculture, Cornell University. Ithaca, N.Y.: Comstock Publishing Co., Inc.; London: Constable & Co., Ltd., 1946. (Pp. xiv + 437, with 12 plates.) 27*s.* 6*d.* net.

Bovine Mastitis. A Symposium. Edited by Ralph B. Little, V.M.D., Department of Animal and Plant Pathology, The Rockefeller Institute for Medical Research, Princeton, N.J., and Wayne N. Plastridge, Ph.D.,

Department of Animal Diseases, The University of Connecticut. McGraw-Hill Publications in the Agricultural Sciences. New York and London: McGraw-Hill Book Co., Inc., 1946. (Pp. xii + 546, with 70 figures and 53 tables.) 35*s*. net.

Insect Microbiology. By Edward A. Steinhaus, Assistant Professor of Bacteriology and Assistant Insect Pathologist in the Agricultural Experiment Station at the University of California, Berkeley. Ithaca, N.Y.: Comstock Publishing Co., Inc.; London: Constable & Co., Ltd., 1946. (Pp. xiv + 763, with 250 figures.) 45*s*. net.

Functional Anatomy of the Mammal. By W. James Leach, Assistant Professor of Biology, Temple University. McGraw-Hill Publications in the Zoological Sciences. New York and London: McGraw-Hill Book Company, Inc., 1946. (Pp. viii + 231, with 96 figures.) 12*s*. 6*d*. net.

Advances in Genetics. Vol. I. Edited by M. Demerec, Carnegie Institution, Cold Spring Harbor, N.Y. New York: Academic Press, Inc., 1947. (Pp. xvi + 458, with 41 figures and 33 tables.) $7.50.

Darwin's Finches. By David Lack, Director of the Edward Grey Institute of Field Ornithology, Oxford. Cambridge: at the University Press, 1947. (Pp. x + 208, with 9 plates, 27 figures and 37 tables.) 21*s*. net.

Apes, Giants and Man. By Franz Weidenreich. U.S.A.: University of Chicago Press; Great Britain and Ireland: Cambridge University Press, 1947. (Pp. viii + 122, with 90 figures.) 14*s*. net.

Annual Review of Physiology, Vol. IX. Victor E. Hall, Editor, Jefferson M. Crismon and Arthur C. Giese, Associate Editors, Stanford University. Stanford University P.O., California: Annual Reviews, Inc. and American Physiological Society, 1947. (Pp. viii + 736, with 1 plate.) $6.00.

Biochemistry of Cancer. By Jesse P. Greenstein, Head Biochemist, Chairman, Section on Biochemistry, National Cancer Institute, National Institute of Health, United States Public Health Service, Bethesda, Maryland. New York: Academic Press, Inc., 1947. (Pp. viii + 389, with 38 figures and 104 tables.) $7.80.

Vitamins and Hormones. Vol. IV. Edited by Robert S. Harris, Professor of Biochemistry of Nutrition, Massachusetts Institute of Technology, and Kenneth V. Thimann, Associate Professor of Plant Physiology, Harvard University. New York: Academic Press, Inc., 1946. (Pp. xviii + 406, with 44 figures and 25 tables.) $6.80.

Recent Progress in Hormone Research. Proceedings of the Laurentian Hormone Conference. Vol. I. Edited by Gregory Pincus. New York: Academic Press, Inc., 1947. (Pp. vi + 399, with 162 figures and 47 tables.) $7.50.

The Anatomy of Lango Religion and Groups. By T. T. S. Hayley, M.A. (Cantab.), M.A. (Oxon.), Indian Civil Service, Director of Publicity and Rural Development to the Government of Assam. Cambridge: at the University Press, 1947. (Pp. xii + 207, with 13 plates and 2 folding plates.) 21*s*. net.

Science and Life in the World, Vol. I: Science and Civilization. The Future of Atomic Energy; Vol. II: Transportation—A Measurement of Civilization. Light, Life and Man; Vol. III: A Challenge to the World. The George Westinghouse Centennial Forum, May 16, 17, and 18, 1946, sponsored by the Westinghouse Educational Foundation, Pittsburgh, Pennsylvania. New York and London: McGraw-Hill Book Co., Inc., 1946. (Vol. I: pp. x + 152, with 11 plates; Vol. II: pp. x + 236, with 12 plates; Vol. III: pp. x + 198, with 28 plates.) 12*s*. 6*d*. each volume.

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SCIENCE PROGRESS

PHOTOSYNTHESIS

By WALTER STILES, Sc.D., F.R.S.

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Of all the problems confronting the plant physiologist none has attracted more attention than that of photosynthesis, the assimilation into the body of the green plant, under the influence of light, of the carbon provided in the carbon dioxide of the atmosphere. This interest is justified, for on photosynthesis depends, with the exception of a few very lowly organisms, all life on this planet. By photosynthesis the green plant is provided with the carbon essential for building up the multifarious carbon compounds which make up its body and which ultimately provide the food of non-green plants and animals, including man, the energy required for the building up of these compounds being provided by sunlight. Not only so, but the development of our industrial civilisation has depended on the utilisation of the energy obtained in bygone ages in photosynthesis by the plants whose remains are now coal.

The realisation of the fundamental importance of photosynthesis for life came gradually during the nineteenth century. The eighteenth-century pioneers, Priestley, Ingen-Housz and Senebier, who established the exchange of oxygen for carbon dioxide by the green parts of plants in light, were mostly concerned with the hygienic effect of this gaseous exchange on the atmosphere, as the very title of Ingen-Housz's work of 1779 witnesses: "Experiments upon Vegetables, discovering their great power of purifying the common air in the sunshine and of injuring it in the shade and at night; to which is joined a new method of examining the accurate degree of salubrity of the atmosphere." It was not until the nineteenth century was well advanced that, owing very largely to the writings of Liebig and Robert Mayer, the significance of the assimilation of carbon from the carbon dioxide of the air in providing food and energy for all living things was generally realised. The demonstration by Sachs in 1862 that in some leaves photosynthesis resulted in the formation of starch, and later work which showed that where

starch was not formed its place was taken by sugar, indicated that the process of photosynthesis consisted in the conversion of carbon dioxide and water into carbohydrate and oxygen, a process involving the absorption of light energy, about 674 kilogram-calories being required to build up one gram molecule of hexose sugar from carbon dioxide and water.

Assuming that the product of photosynthesis is hexose sugar, a reasonable enough assumption though one not even now proved to general satisfaction, we thus obtain the well-known equation

$$6CO_2 + 6H_2O + \text{light energy} = C_6H_{12}O_6 + 6O_2$$

to represent the overall photosynthetic process, the correctness of the equation being indicated by the observed equality of the volume of oxygen given out to that of carbon dioxide absorbed.

The major problem of photosynthesis is to explain in physical and chemical terms how this synthesis of carbohydrate from carbon dioxide and water is brought about in the green plant; to determine, in short, what is usually called the mechanism of the process. Since the establishment of the general character of photosynthesis an unending stream of publications has appeared bearing directly or indirectly on this question. The problem has been attacked from different angles and we now possess a very detailed knowledge of various aspects of photosynthesis. One line of investigation which has been pursued with considerable success has been concerned with the pigments of green plants, those pigments the presence of which is essential for photosynthesis to occur. Another line of work which has yielded much valuable information has dealt with the quantitative relationships between photosynthesis and the various conditions essential for its occurrence. A third line of work, the search for intermediate products in the photosynthetic process, has, on the contrary, yielded disappointingly little information.

As regards the pigments, it had been shown as long ago as 1682 by Nehemiah Grew that the colour of green plants was due to more than one substance, but it was not until the early years of the present century that the separation and identification of the pigments was satisfactorily accomplished by Tswett and Willstätter and Stoll. Tswett introduced the chromatographic method in which an extract of the pigments in an organic solvent such as benzene, petrol-ether or carbon disulphide passes through a column of adsorbent such as dry powdered calcium carbonate, inulin or sugar contained in a glass tube. The different pigments have different adsorption affinities and are adsorbed at different levels, so that the various pigments in the extract become separated into

a succession of layers. By cutting up the whole column into the various layers and extracting each layer with a solvent, solutions of the individual pigments are obtained. From his work on these lines Tswett concluded that green leaves contain two green pigments or chlorophylls, α-chlorophyllin and β-chlorophyllin, and five yellow pigments or carotinoids, xanthophyll α, xanthophyll α', xanthophyll α'', xanthophyll β, and carotene, the last not being adsorbed at all. Willstätter and Stoll, using a method previously employed by Frémy and by Stokes some forty years earlier, that of partition between two non-miscible solvents, separated, as is well known, four pigments, two green and two yellow, the chemical constitution of which they examined and to which they ascribed the following formulæ:

Green pigments:	
Chlorophyll *a*	$C_{55}H_{72}O_5N_4$ Mg.
Chlorophyll *b*	$C_{55}H_{70}O_6N_4$ Mg.
Yellow pigments (carotinoids):	
Xanthophyll	$C_{40}H_{56}O_2$
Carotene	$C_{40}H_{56}$

In the brown algæ the presence of another yellow pigment, fucoxanthin, had been shown spectroscopically by Sorby as far back as 1873. This was isolated by Willstätter and Page in 1914 who ascribed to it the formula $C_{40}H_{54}O_6$. In the red seaweeds other pigments, phycocyanin and phycoerythrin were recognised in addition to the usual green and yellow pigments. So our knowledge of the number of plastid pigments remained for many years. Recently, however, Strain and his collaborators, by spectrographic and chromatographic methods, have produced evidence that the number of chlorophylls in plants must be raised to four. Willstätter and Stoll had shown that in the brown algæ nearly all the chlorophyll was in the form of chlorophyll *a*. Now Strain and Manning conclude that there is a second chlorophyll component in the brown algæ, but that this differs from chlorophyll *b* and is indeed a third chlorophyll which they call chlorophyll *c*. It is said to occur along with chlorophyll *a* in the diatoms and dinoflagellates also. In the red algæ, according to Manning and Strain, a fourth chlorophyll, chlorophyll *d*, accompanies chlorophyll *a*, both chlorophyll *b* and chlorophyll *c* being absent. While the composition of the two new chlorophylls has not been determined, they appear to be closely related to chlorophylls *a* and *b*, but differ in their spectra.

Strain and his collaborators have also separated a number of yellow pigments containing oxygen, thus confirming Tswett's original finding of a number of xanthophylls in the leaf pigments. Willstätter and his co-workers had isolated two such substances to

which the formulæ $C_{40}H_{56}O_2$ (xanthophyll) and $C_{40}H_{54}O_6$ (fucoxanthin) were ascribed. These compounds, called collectively carotinoids by Willstätter, are now called xanthophylls by Strain. According to the latter worker the most important xanthophyll of the leaf is lucein ; this appears to be the xanthophyll of Willstätter and Stoll. An isomer of this, zeaxanthin, is also present among the leaf xanthophylls, while others present include cryptoxanthin, flavoxanthin and violaxanthin with formulæ of $C_{40}H_{56}O$, $C_{40}H_{56}O_3$ and $C_{40}H_{56}O_4$ respectively.

The carotene of green leaves also appears to be a mixture of isomers. According to Mackinney it consists of two components, α-carotene and β-carotene.

The structural formulæ of chlorophylls *a* and *b*, the xanthophylls and the carotenes are all now well established, but it has to be admitted that the knowledge of the molecular structure of these substances has helped very little so far to elucidate the mechanism of photosynthesis.

It is generally agreed that the chlorophylls are responsible for absorbing the light energy utilised in photosynthesis, and it is possible that some of the energy absorbed by the pigments accompanying chlorophyll may also be utilised in the reduction of carbon dioxide to carbohydrate. The most likely explanation of the existence of more than one chlorophyll in the same plant is that light over a wider range of wave lengths is absorbed by two chlorophylls than by one, for the spectra of all the chlorophylls differ. The similarity of the molecular structure and so of the chemical properties of chlorophylls *a* and *b* and probably of *c* and *d* renders it improbable that they play different chemical rôles. For this reason the interesting theory of Seybold that chlorophyll *a* is concerned in photosynthesis and chlorophyll *b* in starch formation is not a very likely one. Seybold pointed out that in *Vaucheria*, where starch is not formed, there is no chlorophyll *b*, while in monocotyledons which do not form starch the ratio of chlorophyll *b* to chlorophyll *a* is less than in starch-forming angiosperms. The older " adaptation " theory, which relates differences in the nature and ratio of the pigments to the different composition and intensity of the light in the various environments appears a more reasonable one.

The investigation of the relationship between photosynthesis and the various conditioning factors, including temperature, light intensity, carbon dioxide concentration, chlorophyll content, largely initiated and inspired by F. F. Blackman and carried out during the first quarter of the present century, emphasised the fact that

photosynthesis involved a non-photochemical reaction as well as a photochemical one, for under conditions of high light intensity when this factor was not imposing a limit on the rate of the whole process, the rate of photosynthesis was affected by temperature in the same way as a purely chemical or "dark" reaction, whereas in low light intensities, when light was limiting the rate of photosynthesis, the latter was proportional to light intensity but little affected by temperature. The dark reaction, indeed, is often designated the "Blackman reaction." Various schemes have been proposed to explain the course of photosynthesis based on the idea that the whole process consists of a chain of reactions, one at least of which is photochemical and one at least a dark reaction. The best known of these is the Willstätter and Stoll theory. According to this, carbon dioxide, having combined with water to form carbonic acid, combines with chlorophyll to form an addition compound. This is a purely chemical reaction. The photochemical stage follows in which, with absorption of light energy, the chlorophyll-carbonic acid compound undergoes isomerisation to a substance of higher energy content and of peroxide structure. By the action of an enzyme this compound decomposes to give chlorophyll, oxygen and formaldehyde; this is the Blackman reaction. The formaldehyde then polymerises to sugar.

A primary difficulty in testing this and any other scheme of the course of photosynthesis lies in the complete absence of any generally accepted information about possible intermediate products of photosynthesis. Support for the formaldehyde hypothesis, so popular for many years and involved in the Willstätter and Stoll scheme, provided by the recognition of formaldehyde in photosynthesising cells, has not stood the test of critical investigation, and the same may be said in regard to other alleged intermediates. Moreover, the Willstätter and Stoll theory appears to be contradicted by recent work on the source of the oxygen given out in photosynthesis. Willstätter and Stoll, as we have seen, considered the oxygen to arise by the breaking down of the carbonic acid, chemically combined with chlorophyll, to formaldehyde and oxygen:

$$\begin{aligned} CO_2 + H_2O &= H_2CO_3 \\ H_2CO_3 &= H.CHO + O_2 \end{aligned}$$

On this view not more than half the oxygen evolved could possibly have come from the water provided; considerations, which it is unnecessary to enter into here, indicate that half the oxygen would indeed come from water and the other half from carbon dioxide. Now in 1941 Ruben and his co-workers in Cali-

fornia examined the photosynthesis of the green alga *Chlorella* provided with water and bicarbonate (and hence carbon dioxide) into which the heavy isotope of oxygen O^{18} had been introduced. The proportion of water and carbon dioxide containing heavy oxygen differed, but it was found that in all experiments the percentage of heavy oxygen in the liberated gas was the same as that in the water provided and was not related to that in the carbon dioxide. This very important finding that the oxygen evolved in photosynthesis is supplied by the water and not by the carbon dioxide has been more recently confirmed by Dole and Jenks. It appears to offer a fundamental objection to the Willstätter and Stoll and similar hypotheses of the mechanism of photosynthesis.

It has for long been recognised that as respiration is an oxidation of carbohydrate with carbon dioxide and water as end products, so photosynthesis, which as far as the overall process is concerned is the reverse of respiration, is a reduction of carbon dioxide. References to photosynthesis as a photochemical reduction process are to be found scattered through the literature, although this aspect of photosynthesis has not been much emphasised until comparatively recent years. It is probably the work of Van Niel in 1931 on the purple sulphur bacteria that has brought this point of view into prominence. In these forms there is a photosynthesis of carbon dioxide to carbohydrate, but the other primary reactant is not water but hydrogen sulphide. The overall process can here be expressed by the equation

$$6CO_2 + 12H_2S = C_6H_{12}O_6 + 6H_2O + 12S$$

further oxidation of the sulphur to sulphate following. This can be regarded as a typical instance of reduction of carbon dioxide by transference to it of hydrogen from the hydrogen sulphide ; carbon dioxide is the hydrogen acceptor, hydrogen sulphide the hydrogen donor (or donator). The normal photosynthesis of green plants can be considered as a similar instance of hydrogen transference in which carbon dioxide is again the hydrogen acceptor and water the hydrogen donor. The exact similarity of the two processes is immediately apparent from the two equations set out below in which for the sake of simplicity the reduction of one molecule only of carbon dioxide is considered :

$$CO_2 + 2H_2O = CH_2O + H_2O + O_2$$
$$CO_2 + 2H_2S = CH_2O + H_2O + 2S$$

Incidentally, this view of photosynthesis as involving the transference of hydrogen from water to carbon dioxide, is in agreement with the observation of the origin of oxygen from water. Just as the sulphur according to the second equation must arise from the

hydrogen sulphide, so the oxygen in normal photosynthesis must similarly arise from the water.

If there were a direct transference of hydrogen from water to carbon dioxide the first product would be formaldehyde hydrate, which on decomposition could give formaldehyde and water:

$$O{=}C{=}O + 4H \rightarrow HO{-}\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}{-}OH \rightarrow O{=}\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}} + H_2O$$

so that formaldehyde could still be an intermediate photosynthetic product. It would seem more likely, however, that the carbon dioxide is first built into a larger molecule before reduction occurs. It also appears probable that four molecules of water are involved in the reduction of one carbon dioxide molecule, because, as pointed out by Rabinowitch, it would be more likely for two molecules of water to provide one hydrogen atom each, while the two remaining hydroxyl groups react to give a molecule of water and a molecule of oxygen, than for one water molecule to lose both its hydrogen atoms.

The implications of Van Niel's theory have been considered in detail in Rabinowitch's recent excellent and exhaustive book on photosynthesis. Rabinowitch points out that photosynthesis can be regarded as a series of oxidation-reductions in which hydrogen is transferred from water, possibly held in some complex, to a first acceptor which is thereby reduced. From this hydrogen is transferred to a second acceptor and so on until finally it is transferred to carbon dioxide, also possibly held in combination. The actual photochemical stage might be anywhere in this series of reactions; it might concern the primary oxidation of water or the final reduction of carbon dioxide, or it might be one of the intermediate reactions. In endeavouring to elucidate the mechanism of photosynthesis it is clearly of first importance to discover which stage in photosynthesis is the actual photochemical one. Rabinowitch, after considering in detail all the possibilities in the light of the available evidence, decides that it is impossible at present to give a definite answer to this question. On the whole he considers that the best working hypothesis is one in which the primary photochemical reaction consists of an oxidation-reduction between eight molecules of one catalyst and eight molecules of a second catalyst; one of the catalysts might be chlorophyll. Half of the oxidised product resulting is concerned in the removal of hydrogen from water, the other half and the whole of the reduced product are

concerned in the reduction of carbon dioxide. The whole scheme is represented by the following series of reactions where A and B denote the two catalysts in their oxidised forms:

$$\begin{aligned} 8HA + 8B &= 8A + 8HB \\ 4A + 4H_2O &= 4HA + 2H_2O + O_2 \\ 8HB\begin{cases} + 4[CO_2] \\ + 4A \end{cases} &\begin{aligned} &= 4B + 4[HCO_2] \\ &= 4HA + 4B \end{aligned} \\ 4[HCO_2] &= 3CO_2 + H_2O + [CH_2O] \end{aligned}$$

the overall equation thus becoming

$$4H_2O + 4[CO_2] = [CH_2O] + O_2 + 3H_2O + 3CO_2$$

The brackets enclosing CO_2, HCO_2 and CH_2O indicate that these groupings are held in combination.

An essential feature of this scheme is what is called energy dismutation represented in the third of the above equations in which the reduction of four molecules of carbon dioxide by four molecules of the reduced catalyst HB is assisted by the re-oxidation of four other molecules of HB by the oxidised catalyst A. In support of this hypothesis Rabinowitch points out that reactions involving energy dismutation do undoubtedly take place in chemosynthesising bacteria, the oxidation of several molecules of substrate being used for the production of a single molecule capable of reducing a molecule of carbon dioxide.

Rabinowitch thus considers it most likely that the photochemical stage of photosynthesis is to be found in neither the primary reduction of carbon dioxide nor the primary oxidation of water, but that these are effected by products, or further derivatives of the products, of the photochemical reaction, and are chemical or " dark " reactions.

As regards the immediate fate of the carbon dioxide on entering into the photosynthetic process we have little information. As already pointed out, we have no definite knowledge of any intermediates in photosynthesis. Ruben and his co-workers have attempted to obtain information on this point by providing *Chlorella* with carbon dioxide containing radioactive carbon. In the dark the absorbed radioactive carbon appeared to enter into the composition of a large molecule containing about 100 atoms, and possibly formed part of a carboxyl group. After exposure of the *Chlorella* to light for a few minutes they were able to show that a whole range of aldehydes, alcohols, acids, amino-acids and other organic substances containing radioactive carbon were not present, and indeed the substance containing the carbon resembled that formed in the dark, except that the radioactive carbon appeared not to be part of a carboxyl group. It may be that the carbon dioxide is first

incorporated into a large molecule containing a carboxyl group and that this is the unknown substance formed in the dark. That in the light the radioactive carbon is no longer in a carboxyl group suggests the possibility that the latter is reduced in the presence of light, and that this might in fact be brought about by the action of the reduced catalyst produced in the primary photochemical reaction hypothesised in Rabinowitch's scheme outlined above.

It must be admitted that this suggestion rests on a very slender body of experimental evidence, but Ruben's work is highly suggestive in indicating how attack on the problems of photosynthesis by the use of radioactive tracers may contribute to the final elucidation of these problems.

All oxidations involve corresponding reductions and if photosynthesis can be regarded as a reduction of carbon dioxide it can equally well be regarded as an oxidation of water, the final oxidation product being oxygen.

We have already observed that according to the Willstätter and Stoll hypothesis the oxygen arises from the decomposition of a peroxide forming part of the chlorophyll-carbonic acid compound after this had undergone isomerisation in the photochemical reaction. It was suggested that this decomposition was effected by an enzyme, possibly a peroxidase. Many writers have found the idea that hydrogen peroxide might be an intermediate product in the oxidation of water in photosynthesis an attractive one, since the enzyme catalase, universal in plant tissues, effects the decomposition of hydrogen peroxide into water and oxygen. However, although many attempts have been made to correlate photosynthetic and catalase activity, it seems clear that no such general correlation exists, while Rabinowitch points out that the considerable amount of energy required for the formation of hydrogen peroxide makes it improbable that it is an intermediate product of photosynthesis.

If the oxygen is not liberated by either peroxidase or catalase action there is still the possibility that it may be effected by an oxidase system. There is not at present any experimental evidence on this point.

As is well known the transference of hydrogen from donor to acceptor in living cells is effected through the agency of the enzymes known as dehydrogenases. Thus the enzyme succinic dehydrogenase effects the oxidation of succinic acid to fumaric acid by the removal of hydrogen from the former by a hydrogen acceptor such as methylene blue or thiamine. The dehydrogenases, as well as the oxidases which oxidise by means of molecular oxygen, are inhibited by various poisons, and information with regard to the

mechanism of photosynthesis may be sought for in determining the effects of various enzyme inhibitors on photosynthesis.

Since Warburg in 1919 first reported that cyanide reduced photosynthetic activity in *Chlorella* much work has been done on the effect of this poison on photosynthesis. Results show considerable variations with different species and any generalisation on the effect of cyanide on photosynthesis is difficult. However, in low light intensities Warburg found photosynthesis in *Chlorella* was insensitive to cyanide, while in strong light the cyanide had an inhibitory effect. This finding at least appears to be generally accepted. Warburg interpreted this as indicating that cyanide does not affect the photochemical reaction which limits the rate of the whole photosynthetic process when light intensity is low, while it does inhibit the dark reaction, which limits the rate of the whole photosynthetic process when the light intensity is high. Among enzymes inhibited by cyanide are various oxidases, catalase and carbonic anhydrase, any of which might conceivably be concerned in photosynthesis. Iodoacetate, an inhibitor of at least some of the dehydrogenases, was found by Kohn to have also an inhibiting effect on photosynthesis, a finding which suggests the participation of dehydrogenases in photosynthesis, although iodoacetate is also an inhibitor of catalase. Urethane, according to Warburg, inhibits photosynthesis of *Chlorella* independently of the light intensity, and so might be supposed to inhibit both the photochemical and the dark reactions of photosynthesis. Warburg's observation has since been confirmed by other workers.

The failure to obtain photosynthesis outside the plant in systems containing chlorophyll and subjected to all external conditions necessary for photosynthesis led to the conception of the protoplasmic factor, a factor in addition to chlorophyll inside the assimilating cell which was deemed necessary for photosynthesis to proceed. Experimental evidence in support of the existence of this second internal factor came from the examination of the development of photosynthetic activity in etiolated seedlings brought into the light. If the seedlings were young enough it was found that a considerable development of chlorophyll could take place before photosynthesis started, thus indicating the need for the development of some second internal factor.

It has been usual to regard the protoplasmic factor as enzymic, and Willstätter and Stoll suggested that it might be a peroxidase catalysing the dark reaction following the photochemical reaction in their theory of the photosynthetic mechanism. From what has been written above it will, however, be plain that the so-called

protoplasmic factor is probably not a single enzyme system, for probably a number of different oxidising enzymes are involved in the overall synthesis of carbohydrate from carbon dioxide and water.

The seat of the photosynthetic process is presumably in the chloroplasts, the granules containing the chlorophyll, and it has for long been an unsettled question whether photosynthesis could occur in chloroplasts isolated from the rest of the protoplasm, or, put in another way, whether the protoplasmic factor can be located in the chloroplast or whether it is a constituent of the cytoplasm. A slight evolution of oxygen by isolated chloroplasts on exposure to light was recorded by Ewart more than fifty years ago, a finding more recently confirmed by Inman. This evolution of oxygen, which is so slight that it can only be demonstrated by the use of bacteria which become luminous in presence of oxygen, does not appear to be accompanied by any absorption of carbon dioxide, and its relation, if any, to photosynthesis was regarded as extremely doubtful.

Some years ago, however, the evolution of oxygen by isolated chloroplasts of *Stellaria media* and *Lamium album* was further examined by R. Hill with the result that a connection between this oxygen production and photosynthesis was rendered more probable. The evolution of oxygen from the isolated chloroplasts was examined by suspending them in a solution of hæmoglobin and observing the production of oxyhæmoglobin from this by means of a spectrophotometer. Hill found that the chloroplasts emitted oxygen in the light, but only in presence of extracts of leaves or certain ferric salts. In particular they brought about a photoreduction of ferric oxalate to ferrous oxalate with evolution of oxygen. They did not make use of carbon dioxide. This work showed that a system containing chloroplasts and leaf extract or a ferric salt could utilise light energy and the work done could be measured in terms of oxygen produced and reduction of a ferric salt. Hill thus regarded the chloroplast as containing a mechanism which absorbs light energy and thereby reduces an unknown substance, not carbon dioxide, with evolution of oxygen. This substance he considered to be capable of rapid reoxidation and to behave, in fact, like a catalyst concerned in hydrogen transference. From later work Hill and Scarisbrick decided that the reaction of chloroplasts with ferric oxalate showed resemblances to the photochemical reaction in photosynthesis and that the system in the isolated chloroplast responsible for the action forms part of the normal photosynthetic process. Further, they concluded from the fact that urethane inhibits the evolution of oxygen by the chloroplasts, while cyanide,

fluoride, azide and hydroxylamine have no effect, that oxygen is formed in photosynthesis in a photochemical reaction not involving carbon dioxide, since Warburg had concluded that in *Chlorella* urethane affected the photochemical reaction while cyanide affected only the dark reaction.

More recently French and Rabideau have examined the quantum yield of oxygen production by spinach and *Tradescantia* chloroplasts suspended in solutions of ferric oxalate and potassium ferricyanide and conclude that as regards its light efficiency the reaction involving oxygen production is not essentially different from that producing oxygen in normal photosynthesis. Kumm and French found that keeping plants in light before removal of the chloroplasts markedly increased the rate of oxygen evolution by the chloroplasts as compared with that from plants which had been previously kept in the dark. They therefore suggest that some unidentified substance, possibly an intermediate in photosynthesis, is built up in the chloroplasts during exposure to light, and that this is necessary for oxygen evolution to take place from the isolated chloroplasts. Hill's work has also been followed up by Warburg and Lüttgens and by Aronoff. Warburg and Lüttgens found that both isolated chloroplasts and disintegrated chloroplasts (the so-called "grana") could reduce not only ferric salts but quinone, the products being hydroquinone and oxygen. Aronoff extended this work to the examination of the effect of the grana on other quinones, such as the naphthoquinones, and found they behaved similarly to quinone, the intensity of the reaction being roughly proportional to the redox potential of the quinone in strong light. A number of other substances such as benzaldehyde and salicylaldehyde produced only small effects. These observations show that the capacity of the chloroplast to reduce substances with evolution of oxygen is not limited to an action on substances containing iron. This does not affect Hill's theory that the evolution of oxygen by chloroplasts *in vitro* is effected by part of the normal photosynthetic mechanism. It does, however, indicate that the unknown substance in the cell which is reduced on absorption of light need not necessarily be an iron compound.

In spite of the enormous amount of experimental work of high quality which has been carried out on photosynthesis during the last forty or fifty years, we are still very far from an elucidation of its mechanism. Plant physiologists have, for many decades, realised that photosynthesis is a complex process, and recent work has only served to emphasise this. Although F. F. Blackman's work of more than forty years ago established the occurrence of both

dark and photochemical reactions in photosynthesis we still have next to no definite knowledge of what these reactions are, or where they occur in the series of reactions which make up the whole photosynthetic process. But the work of the last ten years, although it may not have yielded definite information, has indicated new modes of attack. Among the most promising of these are the use of radioactive tracers as in the experiments already carried out by Ruben and his collaborators, and work on isolated chloroplasts initiated by R. Hill. Development of work along the first of these lines should lead to the discovery of the fate of the carbon in the carbon dioxide absorbed by the green plant, while work along the second line should help towards an analysis of the whole process. Both should aid in the elucidation of the mechanism of the very fundamental biological process of photosynthesis.

THE MOLECULAR STRUCTURE OF COAL

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The classical methods of organic chemistry together with X-ray diffraction studies have given results which permit us to describe, in more or less detail, the molecular structures of complex natural substances such as carbohydrates, proteins, rubbers, etc. Although the molecular nature of coal has been studied intensively for more than a quarter of a century, the picture which can be drawn of its molecular structure is still sketchy and vague, largely because it is much more complex than those of the above-mentioned substances. The word *coal* covers a multitude of different materials ranging from peat to anthracite and few of them are even macroscopically homogeneous. There is, however, little doubt that all are genetically related ; they have been formed from vegetable débris or, in certain less frequent cases, from the remains of marine animal life. The microscope has revealed the presence in coal of vestiges of the original cellular structure of the wood, micro- and mega-spores, cuticles, resins, etc., of the original coal measure forests and swamps. Much of the meticulous work in this field, however, is purely descriptive and, although of considerable importance to the palæobotanist and for the correlation of coal seams, is still without any precise chemical significance. A so-called "coal petrography" has been developed with an extensive and confusing nomenclature based solely on visual observations of polished and transparent coal sections.

The investigations which have revealed most about the molecular structure of coal can be classified under five headings, viz. (1) Studies of natural and artificial coalification ; (2) Solvent extraction ; (3) Thermal decomposition ; (4) Chemical degradation, particularly by oxidising agents, and (5) X-ray diffraction. We shall describe briefly below how these methods have been used and the insight they have provided of the chemical character of coal, and finally give an outline of what is now thought to be the molecular structure of coal.

The Lignin Theory of Coal Formation

Among earlier writers, the idea was widespread that peats, and therefore coals, had been formed from the cellulosic part of vegetable débris, and it was argued from this that their structures must be

based on the furan ring. Franz Fischer and H. Schrader (1921) were the first to question this view and pointed out that cellulose and lignin, the principal constituents of wood, have fundamentally different structures ; the former is aliphatic and made up of furan-like units, whilst the latter contains aromatic rings and acetyl and methoxyl groups. They suggested that during the formation of peat from the plant residues the cellulose has suffered bacterial decay and has been completely converted into carbon dioxide and water. Consequently the proportion of the more stable lignin has increased with time and there has been a concomitant increase in the methoxyl content of the peat. Experiments have shown that such chemical changes occur during the rotting of wood. Brown coal contains only a small percentage of methoxyl and bituminous coal contains none at all. The methoxyl content of a series of geologically related peats and brown coals should therefore show, with age, an increase in methoxyl content, followed by a decrease, whilst the solubility in hydrochloric acid (cellulose) should decrease continuously. Fischer and Schrader supposed that the neutral lignin was first hydrolysed with the elimination of the acetyl groups and the formation of a phenolic, alkali-soluble complex, *viz. humic acid* (see below), which must have a molecular structure similar to that of lignin and initially contain methoxyl groups. The humic acid has gradually undergone molecular condensation, involving perhaps the elimination of water, leading to the formation of the alkali-insoluble material *humin* (see below), which suffered further condensation, with the concomitant loss of water, carbon dioxide and methane ; the aromatic structure of the original lignin remained throughout the whole process of coalification, even in the final bituminous coal.

The following experimental evidence was advanced in support of the above views. Lignin, in contrast to cellulose, yields aromatic degradation products. As rotten wood or peat increases in age, the lignin content increases and there is an initial, related increase in the methoxyl content, followed by a decrease. There is a progressive decrease in the proportion of a peat soluble in concentrated hydrochloric acid as we go deeper into the peat bog. The alkali-soluble humic acid content first increases with the age of the peat and then decreases, as a consequence of humin formation. Hot aqueous alkali converts lignin, but not cellulose, into humic acids containing methoxyl groups which are liberated as methyl alcohol at high temperatures. Although artificial humic acids, prepared from cellulose, on fusion with caustic potash, yield protocatechuic acid and catechol, natural humic acids when treated in the same

way give much larger yields of aromatic acids. The oxidation of cellulose by gaseous oxygen under pressure in the presence of aqueous alkali at 180° C. yields furan carboxylic acids; lignin, on the other hand, yields largely humic acids and finally aromatic carboxylic acids. Debituminised brown coals and also bituminous coals treated in a similar manner yield benzene carboxylic acids, but no furan derivatives: semicokes are likewise converted into aromatic carboxylic acids. Other oxidising agents also transform coals into benzene carboxylic acids, including mellitic acid: wood charcoal can be made to yield as much as 40 per cent. of benzene carboxylic acids. From the results of these pressure-oxidation experiments Fischer and Schrader concluded that there are no furan-ring structures in coal, but only benzene rings.

Lignin tar contains about 34 per cent. of phenols, compared with about 8 per cent. in cellulose tar. Cellulose is relatively quickly attacked and consumed by bacteria, so it is significant that peat beds, even at great depths, are known to contain anaerobic bacteria.

The enrichment of the wax content of peats and brown coals can only have occurred by an appreciable decrease in the proportion of the other substances present, during the rotting process. Vegetable matter poor in lignin (*e.g.* sphagnum, which contains only about 3 per cent. of lignin) yields a peat formed essentially from lignin, and therefore a pronounced increase in the proportion of the plant waxes may be expected.

Although it is not possible to deduce any relationship between brown coal and bituminous coal from their methoxyl contents, a study of the waxes and paraffins formed on destruction distillation gives significant results; *e.g.* montanic acid (C_{28}) can be obtained from both peat and brown coal by solvent extraction and C_{27} paraffins are obtained on distillation. Fischer and Gluud have shown that the solid paraffin in bituminous coal tar also contains the C_{27} hydrocarbon.

The Lignin Theory does not exclude cellulose from some part in coal formation; it merely insists that it does not play the decisive rôle which had hitherto been assumed. Lignin is present in fir to about 28 per cent.; in oak to about 37 per cent., and in nut shell to about 47 per cent.; the balance is largely cellulose. The Lignin Theory is summarised in Figs. 1 and 2; these suggest that the humins decompose at about 500° C. giving off phenols, whilst the wax-like bitumen fraction yields hydrocarbons similar to petroleum. This mixture of phenols and mineral oil forms the primary tar; if this is heated to about 800° C., as it is during the glare-scale destructive distillation of coal, cracking occurs in the

presence of hydrogen to an extent dependent upon the prevailing conditions. Benzene and smaller amounts of toluene and xylene are formed from the phenols, whilst the mineral oil part of the primary tar is largely converted into gas. According to Fischer, the benzene and other aromatic constituents of coal tar derive essentially from the lignin of the original plants.

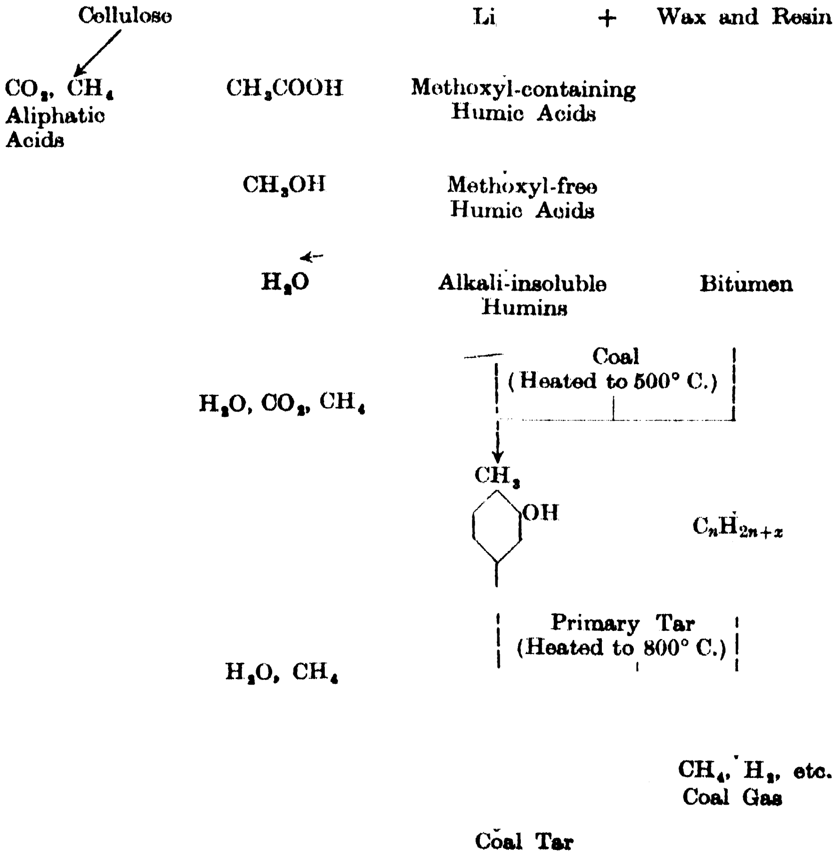

FIG. 1.—The Lignin Theory of coal formation.

The Lignin Theory has been criticised on the ground that the disappearance of cellulose would involve the disappearance of the original cellular structure of the wood, which can be clearly seen in many mature coals. Fischer pointed out, however, that cellular structures can be detected in lignin prepared by the Willstätter method and that cell membranes contain lignin. E. Berl (1928–33) has questioned the correctness of Fischer's views, largely on the ground that it is possible to make coal from cellulose in the labora-

tory. F. Bergius (1913) heated cellulose, and also peat, in an autoclave with water to temperatures up to 340° C. and concluded that the products were similar in character to coking coals and that these experiments indicated the manner in which bituminous coals were formed in nature. Fischer and Schrader heated cellulose and lignin with water under pressure, in the presence of barium carbonate, to temperatures of 200° and 300° C.; the cellulose was converted, in increasing measure, into water-soluble compounds

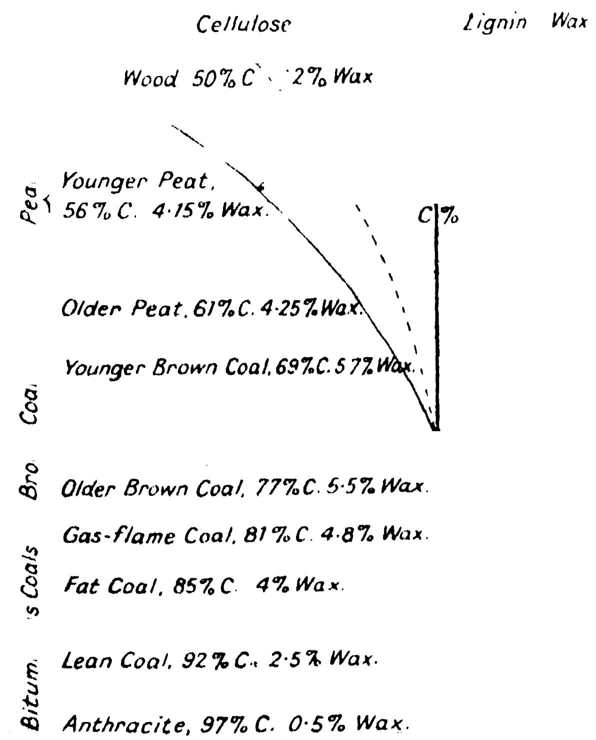

FIG. 2.—The Lignin Theory of coal formation.

and gases, whilst the lignin showed considerable powers of resistance. Extensive experiments on the artificial "coalification" of cellulose, lignin, resins and waxes in both neutral and alkaline media at high temperatures (150°–350° C.) and pressures were carried out by Berl and co-workers. At 350° C. cellulose gave a yield of solid product of 30 per cent., whereas lignin gave 65 per cent.: this difference is not surprising in view of the greater carbon content of the lignin. The above workers had no unequivocal test for a bituminous coal and, although some of their products on

carbonisation showed both caking and swelling properties, subsequent X-ray examination (Blayden, Gibson and Riley, 1945) showed them to be more closely akin to peats and brown coals than to bituminous coals.

Coal Resins

Peat bitumen is similar in character to brown coal bitumen and consists principally of resinous and waxy materials; the proportion of material extractable by organic solvents (usually a mixture of ethyl alcohol and benzene) varies between wide limits. In lignites rich in volatile matter (*Schwelkohlen*) it is on the average between 15 and 25 per cent. Bituminous coal bitumens are fundamentally different, for they show little or no resinous or waxy characteristics. H. Potonié (1920) has explained this by the theory that the Carboniferous plants did not excrete resins and waxes of the montan wax type. C. Engler and J. Tausz (1921), however, hold that the soluble brown coal bitumens, because of polymerisation, have become insoluble during the course of coalification. But Berl and Schmidt have shown that the artificial coalification of resins and waxes at temperatures even up to 400° C. does not bring about any fundamental change in the character of these substances. The permanent character of the resins is also indicated by the fact that they can be detected in bituminous coal, although not so easily as in peat and lower rank coals. According to R. V. Wheeler and R. Wigginton (1922) their properties, as compared with the original vegetable resins, have changed; they have become very much less soluble in ethyl alcohol, ether, etc., and have a higher carbon and hydrogen content than the parent coal. W. Francis and Wheeler (1926) isolated, from a Hamstead vitrain, yellow rods of resin, varying in length up to about 0·02″ and with a diameter about one-tenth of the length. R. Thiessen (1924) has also identified resins of microscopic size in a number of American coals. Little or nothing is known about the molecular structure of these resins.

Sapropelite Coals (Bogheads and Cannels)

Geological and petrographic investigations have shown that some coals have been formed from the débris of the higher plants; others, however, appear to have their origin in the residues of microplants (*Ölalgen*). The former, which include both brown coals and bituminous coals, have been termed *humus coals*, and the latter *sapropelite coals*. According to H. Potonié, the sapropelite coals were formed from the "rotten slime" (*Faulschlamm*; Greek, *sapros* = rotten) which often accumulates in swamps.

G. Stadnikoff (1930, 1931) has suggested that this difference in the origin of the humus coals and the sapropelite coals is reflected in their different chemical characters. Following Fischer, he believes that the humus coals consist of bitumens and humus derived from lignin and that it is the humus material which gives phenols on destructive distillation. The sapropelite coals, on the other hand, consist of fatty acids and their transformation products and on dry distillation do not give phenols but paraffins and naphthenes. The primary tars from humus coals are rich in phenol ; *e.g.* the primary tars of genuine boghead coals contain about 2 per cent. of phenols. Many coals are probably of mixed origin and contain both humus and sapropelite material.

The Swelling of Bituminous Coals

An interesting and commercially important property of certain bituminous coals is their power of yielding, on carbonisation, strong coherent cokes. This property, which is related to the rank of the coal, can be assessed approximately by the Crucible Swelling Test, which consists in rapidly heating over a bunsen burner one gram of the finely divided coal contained in a covered silica crucible. Fig. 3, Plate I, shows the results obtained by means of this test, in the case of fourteen coals covering a wide range of rank. The coal of lowest rank (60 per cent. of volatile matter) gave, on carbonisation, a non-coherent powder : the second coal of somewhat higher rank (42 per cent. volatile matter) gave a non-swollen, friable coke button. Passing up the rank series, the coke buttons obtained were more and more swollen and reached a maximum size with coals containing just over 20 per cent. of volatile matter. Still higher up the series, the amount of swelling decreased progressively until finally coals containing about 11 per cent. of volatile matter gave non-coherent powders. Why should this swelling property gradually develop and then disappear as the coal increases in rank ? Solvent extraction experiments have shown that this swelling and agglutinating property is due to the presence in the coal of substances which can be extracted by solvents such as pyridine, benzene, tetralin, etc. Fischer and Schrader have suggested (see Fig. 1) that the coking bitumens have been formed in the course of geological time from the waxes and resins present in the original vegetable matter. X-ray diffraction studies of coals and coal fractions have shown, however, that the coking coal bitumens consist of substances which bear little or no structural relationship to the waxes and resins.

This X-ray evidence can be summarised briefly as follows.

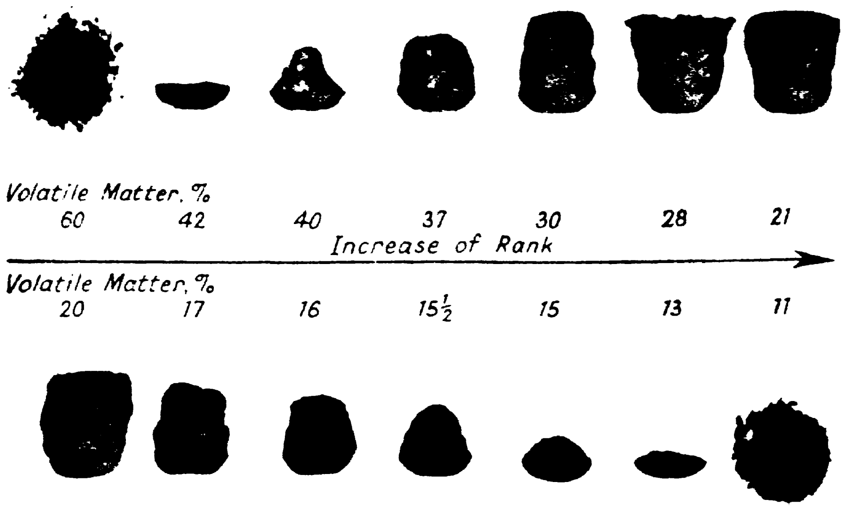

Fig. 3.—Variation with rank of the swelling properties of coal.

The inner and more intense diffraction halo in the X-ray powder photograph of a coal is highly diffuse. If samples of the coal are heated to progressively higher temperatures and the products examined by X-rays, the half-peak width of this diffraction halo (*i.e.* its width at half the peak intensity) suffers systematic variation. It first shows progressive sharpening up to 550° C. followed by broadening up to 900° C. and a subsequent sharpening at still higher temperatures. The diffraction half-peak width can be used to calculate the height (*c*-dimension) of the hypothetical, average cylindrical crystallite, *i.e.* the statistical unit of the ordered part of the coal structure. If this *c*-dimension is plotted against carbonising temperature, a bituminous coal gives rise to a curve which shows a more or less pronounced maximum (12 to 20 Å) in the neighbourhood of a carbonising temperature of 550° C. Not all carbonaceous substances behave in this manner ; many, particularly those containing a large proportion of oxygen such as cellulose and lignin, give chars showing a constant *c*-dimension (about 9 Å) over a wide range (400°–1200° C.) of carbonising temperature. Coals which contain a high proportion of coking coal bitumens show pronounced maxima in their *c*-dimension curves, particularly if the carbonisation is carried out slowly. These phenomena indicate that, whereas chars from cellulose and lignin and other similar substances possess a rigid lattice structure, the bituminous coal bitumen molecules are sufficiently thermally stable and mobile to undergo a kind of unidimensional crystallisation in the temperature range up to 550° C., which results in the sharpening of the inner diffraction halo. The fact that the bitumen molecules are thermally stable and retain their mobility and individuality up to temperatures which may be as high as 550° C. suggests that they are large, polynuclear aromatic molecules ; they must be highly carbonaceous but must contain some oxygen or nitrogen, otherwise they would volatilise rather than carbonise at 550° C. The proportion of oxygen or nitrogen is probably critical. The unidimensional crystallisation suggests also that the molecules have a more or less lamellar shape. The discussion of the further course of the *c*-dimension curve above 550° C. is outside the scope of this paper.

The residual coal, *i.e.* the residue left after extraction of the bitumen with an organic solvent, shows an X-ray crystallographic behaviour quite different from that of the soluble bitumen fraction. As the carbonising temperature increases, the *c*-dimension shows a progressive, more or less slight, decrease and passes through a minimum at about 900° C., above which temperature there is a pronounced increase. This behaviour is more reminiscent of that

of cellulose and lignin chars than of the coking coal bitumens, and suggests that the residual coal has a three-dimensionally cross-linked structure.

A direct proof of these views concerning the molecular nature of coking coal bitumens is not easy. It has been shown, however, that dibenzanthrone, Fig. 4 ($C_{34}H_{16}O_2$, molecular weight 456; C, 89·47; H, 3·51; O, 7·02 per cent.), and certain other pure

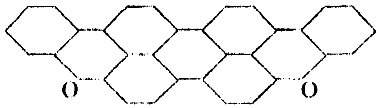

FIG. 4.—Dibenzanthrone.

organic compounds, all of which fulfil the above specification, on carbonisation show caking and swelling properties and X-ray crystallographic changes which are remarkably similar to those exhibited by a bituminous caking and swelling coal. To what extent this is a reflection of molecular similarity it is not yet possible to state, but it appears reasonable to suppose that similar types of molecules are involved, although differences in molecular weight may obtain. The property possessed by coking coals of forming strong and coherent cokes on carbonisation depends upon the high-temperature film-forming properties of their bitumens, *i.e.* upon their high-temperature agglutinating power. Certain organic compounds possess agglutinating properties at lower temperatures, *e.g.* starch when heated forms a semi-liquid substance which consists of a tangled mass of complex pyranose chains, which still contains a relatively high proportion of oxygen even when the chains have lost their molecular individuality and the mass has set (cross-linked) to a char at a relatively low temperature (about 250° C.). As the temperature is still further increased, this oxygen is progressively evolved as oxides of carbon, with a consequent weakening of the solid residue and the final formation of a weak and friable carbon.

How have these coking coal bitumens been formed in nature? They bear no chemical relationship to the resins and waxes present in the original vegetable débris, and it is unlikely that the development of caking and swelling properties in the coal is in any way connected with the presence of such substances in the parent carbonaceous material. It is more reasonable to suppose that the formation of coking coal bitumens is an essential stage in the anaerobic degradation of vegetable débris under certain favourable conditions. The rapid maturing of young coals (which contain a high

proportion of oxygen), brought about by an excessive rise in temperature, would result in the formation of rigid "carbon" crystallites rather than of independent bitumen molecules. One would not expect to synthesise a vat dyestuff, or a similar compound, merely by the pyrolysis of lignin or cellulose; it therefore appears improbable that coking coal bitumens have been formed by any rapid degradation process. The general tendency in a mass of decaying organic matter will be for the system to lose free energy by a process of aromatic condensation resulting in the formation of progressively larger polynuclear aromatic molecules with a concomitant loss of resonance energy. This will result in a progressive weakening of the bonding of any peripheral groups and offers an explanation of the gradual evolution of methane and carbon dioxide during coalification. Such changes will eventually lead to the formation of large polynuclear aromatic molecules possessing the critical proportion of oxygen, *i.e.* to the formation of coking coal bitumens. The essential requirement of such a natural synthesis is that it should occur extremely slowly under anaerobic conditions, otherwise rigid carbon crystallites would be formed.

There is definite X-ray evidence that certain of the most mature coals, *viz.* the anthracites, have passed through a coking coal stage; *e.g.* South Wales anthracites must at one time have contained a high proportion of bitumen. It further appears probable from the X-ray evidence that the decrease in the proportion of coking coal bitumens as the coals mature has also been brought about by mountain-building forces.

FUSAIN

Fusain is one of the banded constituents of bituminous coal and occurs in irregular wedges lying along the bedding planes. It is very friable and readily breaks down to a powder which gives a black streak. The microscope reveals in fusain the original cell structure of the wood, but the cell walls are generally blackened and thickened and often split. Fusain has been formed from woody fragments which have undergone a form of degradation different from that obtaining in the case of bright and dull coals and which has led to the formation of a charcoal-like product. Its moisture, volatile matter and hydrogen contents are lower than those of the accompanying bright and dull coals; it yields a very small pyridine-soluble fraction and gives very little tar on destructive distillation. It has been suggested that fusain is a charcoal formed in forest or bog fires. Another view is that it has been formed from vegetable matter, which before burial had been subjected to conditions dif-

ferent from those obtaining in the formation of bright and dull coals; *e.g.* it may have been subjected to dry rot as a result of the parent vegetable matter protruding above the level of the water in the coal swamp.

The most significant fact about fusain is its low bitumen content. X-ray examination has shown that it gives a *c*-dimension curve of the cellulose char type, *viz.* the *c*-dimension remains constant at about 12 Å over a wide range of carbonising temperature. This suggests either that a rigid crystal structure has been formed by an excessive rise in temperature whilst the parent material still contained a relatively high proportion of oxygen, or that possibly the degradation of the parent carbonaceous matter has occurred under prolonged aerobic conditions.

Humin and Residual Coal

Bitumen makes up only part of a coal; the remainder of the coal, *i.e.* that part which is insoluble in organic solvents, is termed the *residual coal.* It contains a proportion of oxygen higher than that present in the accompanying bitumen and it is probably structurally related to that group of complex substances known as the humic acids.

Soil humus is known to contain about 40 per cent. of humic acids and, in spite of many exhaustive investigations, its molecular structure is still obscure. Humic substances are formed during the natural decomposition of wood, cellulose, lignin, *etc.*, and are characterised by solubility in caustic alkali; humic acids are precipitated on the addition of excess mineral acid to the caustic alkali solution. Artificial humic acids can be prepared by a variety of methods and, although they show a certain similarity to the natural products, there is no proof of close chemical similarity. The acidic character of humic acids is shown by their power of salt formation; the ferric and lead salts are basic in character and not readily dispersed, whilst the silver salt, in contrast, has a tendency to pass into colloidal solution. The capacity of humic acids of forming adsorption complexes with salts makes exact studies difficult. According to their behaviour with aqueous alkali, humic substances are classified as *humic acids* and *humins*; the former are easily soluble in cold aqueous alkali, whilst the latter only dissolve on heating. The different alkali solubility of the humins has been interpreted by J. Marcusson (1927) in the sense that these substances are dehydration products or anhydrides of humic acids. The decrease in the solubility in aqueous ammonia which occurs when the acid is dried at 105° C. (W. Schneider and A. Schellenberg,

1920) is ascribed to an alteration in the colloidal state of the substance and not to anhydride formation.

Humic substances when brought into contact with salt solutions display the property of hydrogen ion- or base-exchange. There seems to be little doubt that humic acids must be regarded as complicated aromatic carboxylic acids; besides carboxyl and phenol groups, upon which the acidic properties depend, other characteristic groups, such as carbonyl and other oxygen-containing groups not yet identified, are also present. The composition of humic acids obtained from peat or brown coal is not as constant as that of a well-defined compound, but in many cases approximates to the empirical formula $C_5H_4O_2$; the nitrogen and sulphur always found in natural humic acids are now usually regarded as adventitious impurities.

In an investigation of Italian brown coals, I. Ubaldini (1937) found that carboxyl acidity is a function of their degree of humification; it increases with the extent of the transformation of the original vegetable matter into humic substances and subsequently decreases gradually with the progress of coalification. Phenolic groups, on the other hand, are already present in the parent substance of the brown coals and the proportion decreases gradually during the humification process; they are still present in significant amounts in coals intermediate in rank between brown coals and bituminous coals. Ubaldini suggested the following approximate formula for humic acid:

$$C_{78}H_{52}O_5 \begin{cases} (COOH)_8 \\ (OH)_7 \\ (CO)_2 \end{cases}$$

R. C. Smith and H. C. Howard (1935) carried out equivalent and molecular weight determinations on samples of humic acids prepared from a bituminous coal by nitric acid oxidation. A sample dried from room temperature up to 150° C. gave an equivalent weight (electrometric titration) of 232 to 248. Cryoscopic determinations in pyrocatechol gave a molecular weight of 300 to 360 for specimens dried from 150° to 200° C., but only 220 for those dried at 25° C. Acetone-soluble and -insoluble fractions gave equivalent weights of 210 to 277 and molecular weights of 190 to 240 and 260 to 300 respectively in pyrocatechol. The ethyl alcohol-soluble and -insoluble fractions of the ethyl esters gave molecular weights of 380 to 315 respectively in pyrocatechol. These authors suggested that humic acids consist of molecular aggregates, which dissociate in polar solvents, but resist the disruptive action of heat.

Osmotic pressure determinations (C. L. Arnold, A. Lowy and R. Thiessen, 1935) have indicated molecular weights of peat humic acids as high as 2700.

According to W. Schneider (1922) most of the German earthy brown coals can be more or less completely dissolved by a sufficiently long treatment with hot caustic alkali. The Upper Bavarian pitchy brown coals, which are of Tertiary origin and intermediate in character between the common brown coals and the younger bituminous coals, according to E. Erdmann (1924), are much less soluble in alkali and contain a much smaller proportion of readily soluble humic acids and a higher proportion of humins and residual coal than the soft brown coals. This decrease in alkali solubility with rank gave rise to the theory that the humins are formed from the humic acids by the development of acid anhydride, ether and lactone groupings: the further change to residual coal (*Restkohle*) is caused by decarboxylation and further anhydride formation. If these processes are intra-molecular then they will involve molecular condensation. Drying at 100° C., heating in air at 250° C., heating in paraffin oil or in benzene under pressure, or by superheated steam, all convert humic acid into humins which can only be brought into solution again by heating in aqueous alkali or even only in molten caustic soda.

W. Fuchs (1928) conceived humins as substances closely related to the humic acids, but containing no carboxyl groups, and ascribed to them the structure of reduced oxy-carboxylic anhydrides. Stadnikoff (1931) considered the humins to be intermediate products between the free humic acids and the humus coals and suggested the possibility of a purely colloidal process being responsible for the decrease in alkali solubility, *viz.* the ageing of the humic acid gel, leading to the formation of a difficultly peptisable humic acid, without any essential change in the chemical nature. The three characteristic constituents of ordinary brown coal, *viz.* humic acid, humin and residual coal, have been termed by H. Stach (1933) α, β and γ humic acids respectively; they differ from one another only in their solubility in aqueous alkali, otherwise specimens from the same coal show very close chemical relationship. Thoroughly extracted (debituminised) α and β humic acids, on destructive distillation, yield very little tar, whereas the γ humic acids, on the other hand, give large yields of tars containing carboxylic acids and paraffins. It cannot therefore be concluded that sapropelitic and resinous materials (removed by the extraction) are exclusively concerned in the formation of the residual coal.

W. A. Bone and co-workers (1927–37) studied the alkaline per-

manganate oxidation of residual coals obtained by the benzene-pressure extraction of coals covering a wide range of rank, and concluded from their results that the "main coal substance" (*i.e.* the residual coal) has an essentially benzenoid character, which increases progressively throughout the lignin→peat→coal→anthracite series, a conclusion based upon the progressively greater yields of benzene carboxylic acids obtained as the rank of the residual coal oxidised increased.

Although the residual coal obtained from a mature coal is largely insoluble in alkali, it has long been known that gaseous oxygen or aqueous oxidising agents react with such coals, forming a product which dissolves in aqueous alkali; apparently the humins and humic acids can be regenerated by oxidation.

Conclusion

An attempt has been made above to give a picture of the molecular structure of coals in terms of two constituents, *viz.* (*a*) the bitumen, *i.e.* that part of the coal soluble in organic solvents, and (*b*) the residual coal. In the younger coals, *i.e.* the peats and brown coals, the bitumens consist of resins and waxes similar in chemical character to the resins and waxes excreted by certain modern plants, whereas the bituminous coals contain bitumens which are essentially aromatic substances of high thermal stability and are responsible for the caking properties of these coals; some resinous and paraffinic material is also present in these bitumens. The residual coal of the peats and brown coals is more or less readily soluble in alkali and is closely related to the humic acids and humins, whereas that of the bituminous coals is only soluble in alkali after a preliminary oxidation. The residual coal has probably a complex three-dimensionally cross-linked structure and its aromatic character is known to increase with the rank of the parent coal. In the mature bituminous coals it appears to be closely related crystallographically to anthracite.

Although we have described coal in terms of bitumen and residual coal, they should not be conceived as two distinct entities: in bituminous coals they are very intimately related and closely associated. It is possible by relatively mild hydrogenation (F. Fischer, K. Peters and W. Cremer, 1933) to increase the proportion of extractable bitumen or pseudo-bitumen. Hydrogenation of a residual coal gives further quantities of extractable bitumen (W. E. Bakes, 1933; T. Shimmura and H. Nomura, 1933). B. S. Biggs (1936) found that the humic acids obtained by oxidising with nitric acid the ether-soluble and -insoluble fractions of the benzene extract

of a bituminous coal, and the insoluble residue from this extraction, were all similar ; mild catalytic reduction at 350° C. of the benzene-insoluble residue gave pseudo-bitumens indistinguishable from those extracted from the original coal. These results suggest that the hydrogenation brings about some kind of depolymerisation of the complex, cross-linked residual coal with the formation of bitumen-like material.

Nothing has been said above concerning the difference in molecular structure between bright coals and dull coals. Certain dull coals, *e.g.* Yorkshire durains, are devoid of any swelling properties, presumably because of the low proportion of coking coal bitumens present. It is not possible, however, to generalise with regard to this ; the detailed investigations of K. Drees and G. Kowalski (1934) of Upper Silesian bright and dull coals, covering a wide range of rank, indicate surprisingly small differences in the respective chemical and coking characteristics of these two classes of coals taken from the same seam. The explanation of this probably lies in the higher proportion of sapropelitic material in the Upper Silesian coals as compared with the Yorkshire durains.

Because of their complexity and heterogeneous character, much further detailed investigation is necessary for the fuller elucidation of the molecular structure of the less-mature coals. In the case of the more mature bituminous coals and the anthracites, however, there appear to be good prospects that X-ray diffraction methods will continue to yield results which will throw still more light on their ultimate structures.

THE EYE AS A DETECTOR OF LIGHT. QUANTUM FLUCTUATIONS IN VISION

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Outline of the Problem

It is a most common observation in biology that a living organism does not always give the same response to a physical stimulus when the stimulus is applied to the organism repeatedly. In the past it was generally assumed that the variability of the response was certainly due to changes in the organism itself and not to variations in the stimulus. The main object of this paper is to discuss a particular case in which there is strong evidence that this conclusion does not apply. In the experiments to be described—the stimulation of the retina, and of the organism, by light—it will be shown that the sensitivity of the organism may be constant, while the physical stimulus itself must be expected to undergo unavoidable variations from one trial to another. These physical fluctuations are due to the quantum nature of light. Their magnitude is such that they can explain quantitatively the variability of response observed under the particular conditions of the experiments.

In order to give a more concrete idea of the problem, an experiment may be briefly outlined. When our gaze is fixed on a particular point of the outside world, the image of this point falls into the *fovea centralis* of the retina; and an image of the outside world is spread on to the whole of the retina by the dioptric system of the eye. Let us imagine then that we are in a dark room containing only two small sources of light. One of these is a continuous point source. The other is intermittent, giving from time to time a light flash of constant duration and intensity. We fix our gaze on the continuous source—the fixation point. In this way, the image of the fixation point is formed in the fovea and the retina is therefore kept in a constant position. Then, from time to time, the second source sends a flash of light and its image is formed in a peripheral part of the retina, which is the same for each flash.

The periphery of the retina contains both rods and cones but, as is well known, the rods are generally the more important when small quantities of light are under consideration [1], and we shall

here disregard the cones. The light of a flash given off by the intermittent source is partly absorbed by the visual purple which is contained in the rods of the region covered by the small retinal image of the source. It is this light fraction absorbed by visual purple which is effective in stimulating the rods and which thus constitutes the physical stimulus acting upon the organism. (The fraction of the light which passes through the rod layer without being absorbed is eventually stopped by the black pigment lining the walls of the eyeball; it is there transformed into heat and lost as far as the visual process is concerned.)

Now it might be thought that in such a way it would be possible—by using special precautions—to deliver to a given part of the retina exactly the same amount of light each time a flash is emitted, the retina absorbing a constant fraction of the constant amount of light striking it. It will be seen presently, however, that it is not so.

It is impossible to make the retina absorb the same amount of light, that is, the same number of quanta, in each trial. Consequently, even in the absence of any biological variations, the response of the organism to the flash cannot be expected to be always the same. Near the limit of visibility the flash will sometimes be seen, and sometimes not.

To make the meaning of this clear, a simple analogy might perhaps be used. There are slot machines which deliver a ticket when, say, 6 pennies have been inserted into the slot. As a rule, when a "stimulus" of 6 pennies is applied to a machine of this kind, it will always give, as a "response", a sixpenny ticket. Imagine now a machine such that sometimes we do not get our ticket after inserting 6 pennies but we get it only after inserting more than 6, say, 9 pennies. On the other hand, imagine that this machine sometimes delivers a ticket after we have inserted less than 6 pennies, say, 3 pennies or 1 penny. The obvious conclusion would be that the state of the machine varies from time to time. Sometimes unused pennies may have been left in it; so that its "threshold," that is, the number of pennies which must be inserted to obtain a response, is then lower than 6. At other times the mechanism of the machine may have become "sticky": the machine is then less sensitive and needs a greater stimulus to give a response; its threshold is higher than the normal threshold of 6 pennies.

If we insert 6 pennies in the slot and sometimes get our ticket, while at other times we do not get it, we have no doubt that the cause of this irregularity must be in the machine, because we know that we have placed into the slot machine exactly 6 pennies each

time. In what concerns the stimulation of the retina by light, however, the whole point is that it is physically impossible to deliver to it exactly the same amount of light, say, 6 quanta, in each trial. And in this case we are therefore not justified in concluding that the variability of the response—that is, the fact that at the limit of visibility a light is sometimes seen, and sometimes not—is necessarily due to a variability of the organism.

As is universally known, the modern theories of quantum physics state that every emission or absorption of light by matter can be traced down to individual processes, each of which involves one single quantum having an energy $h\nu$ (h being Planck's constant of action and ν the frequency of the radiation which is considered).

This means, in other words, that light behaves in its interaction with matter as if having a corpuscular nature. The filament of an electric lamp does not emit a smooth, homogoneous flux of light. On the contrary, it emits light rather in the way a machine gun emits bullets. In a given time, the filament emits a discrete number of these bullets, or quanta.

During one second, an ordinary electric bulb emits a large number of quanta of visible light. The number is of the order of 10^{19}. In any particular second, therefore, the filament may emit for instance, a number of quanta such as

10,281,183,942,006,252,729 quanta,
or 12,073,461,023,419,493,146 quanta,
or 12,073,461,023,419,493,147 quanta ;

that is, always an integer number of quanta. But the filament will *not* emit fractions of quanta, such as for instance

12,073,461,023,419,493,146·36 quanta.

The same applies to absorption of light by matter. When a beam of light passes through a layer of absorbing substance, for instance a coloured liquid, a discrete number of quanta are absorbed by the substance. The least amount of light which can be absorbed is one quantum $h\nu$. The amount of light absorbed therefore is either 0 or 1, 2, 3, 4, 5, . . ., or any integer number of quanta. A fraction of a quantum cannot be absorbed.

Now, needless to say, the energy of one quantum of visible light is very small. For a wavelength $\lambda = 0{\cdot}510\,\mu$ (the wavelength of blue-green light), for instance, it is

$$h\nu = 3{\cdot}84 \times 10^{-12} \text{ erg.}$$

And, as has been seen, the number of quanta emitted by ordinary sources of light, such as electric bulbs, is correspondingly very

large. This number is so large that it might have been thought that the quantum emission or absorption of light is of purely theoretical importance and has no consequences or, at least, no direct consequences, observable in experiments—for the same reason as Brownian movement is generally not observed in the case of ordinary macroscopic particles of matter made up of a very large number of molecules.

It will be seen presently, however, that the sensitivity of the eye is extremely high, so high in fact that the above remark is not applicable in its case. For a number of quanta of the order of 10 only, absorbed by the retina, can produce a visual response of the organism. Under such conditions, physical fluctuations of considerable magnitude take place, from trial to trial, in the number of quanta actually absorbed by the retina.

These fluctuations occur because the quantum processes of emission and absorption are individual independent processes. A fraction of a quantum cannot be absorbed. All quanta—of light of one frequency—are the same. A quantum will either be absorbed entirely by the retinal rod layer or will not be absorbed by it. But it cannot be predicted which will be the case. There is merely a certain probability of the quantum being absorbed by the retina. It follows that different numbers of quanta can be absorbed in different trials; for instance, it may happen by chance that none of the quanta be absorbed. In fact, there is a finite probability of any integer number of quanta being absorbed, and this probability can be calculated, on pure probability grounds, from a knowledge of the average number of quanta absorbed by the retina under constant experimental conditions. In contradistinction to this it is clear that if light were emitted and absorbed as a continuum, the retina could absorb a constant fraction of the light from the source and this amount of light absorbed would then be exactly the same in each trial.

Sensitivity of the Eye

Laboratory measurements show that, through a non-absorbing atmosphere, a man could see a standard candle at a distance of about 25 kilometres [2]. (Incidentally, it can easily be calculated from this result that a powerful searchlight directed from the moon to the earth should be visible here with the naked eye [3].)

The dimmest stars which can be seen with the naked eye, under special conditions of observation, are those of magnitude 8·5 [4]. Such a star produces at the eye an illumination which is about 10^{-14} times the illumination produced by the sun [3].

In terms of energy, the least flux of radiation which must strike the eye in order that a point source of light be seen is of the order of

$$10^{-9} \text{ erg per second [2, 5].}$$

In comparison, sensitive thermopiles need a flux of about 10^{-2} erg/sec. to give a galvanometer deflection [3].

Other detectors of light, such as certain photon counters, are more sensitive than thermopiles. It is still an open question what the limit of performance of these detectors exactly is, and whether it really compares with that of the eye.

Wien, a student of Helmholtz, appears to have been the first to have estimated, in 1888, the value of the minimum flux of energy which the eye receives from the faintest visible stars [6]. During the same year, Langley, the American astrophysicist, was using the bolometer—which he had just invented—to measure the absolute threshold of the eye in the laboratory [7].

Wien had made measurements of the sensitivity of the ear [6, 8] and he wanted to know whether the eye was as sensitive as the ear. In fact, both sensitivities are of the same order of magnitude, 10^{-9} erg/sec. It may be remarked that in the case of hearing, this energy flux corresponds to an extraordinarily small amplitude of the air waves, namely, about 10^{-8} cm. or 1 Ångstrom unit, which is the order of the dimensions of the air molecules themselves. It may be pointed out that the problem of the limit of performance of the ear is worth re-examining. This should be done in conjunction with the theory of Brownian movement and the theory of fluctuations evolved by Smoluchowski and Einstein. It would appear that, so to speak, we are possibly not very far from being able to hear the bombardment of the air molecules on our eardrum [9].

Coming back to the eye, as we have seen, a point source of light sending into the eye an energy flux of about 10^{-9} erg/sec. can be seen. It will be remembered that 1 erg is approximately equal to the energy necessary to lift a mass of 1 milligram to a height of 1 centimetre. An amount of light equal to one thousand-millionth of this small quantity per second is thus enough to produce a visual response. In terms of quanta, this minimum flux of light corresponds to a few hundreds of quanta per second.

Interesting as this information may be from a general and from a practical point of view, it remains vague from the physiological point of view. For it leaves undefined what region of the retina is stimulated by the faint luminous image formed on it. Furthermore, the time relationships are also left undefined, for the

second is of course an arbitrary unit without natural physiological significance.

The existence of the saccadic movements of the eye must be borne in mind in this connection. Under ordinary conditions of vision the eye, after moving very rapidly, stops in a given position for a duration of the order of one-tenth of a second. Then it moves rapidly to another position ; this is followed by another brief stop ; then on again, and so on. The duration of one of the stops, 0·1 second, is of the same order as the " retinal action " time.

The " retinal action time " is the time during which summation of the effects of light occurs in the retina [10]. When the exposure is shorter than the retinal action time, all that matters for the outcome of the experiment is the total amount of light received by the retina, that is, the product of the light intensity by the exposure time.

It appears that the saccadic eye movements must introduce complications of the following kind. When we look at a star in an ordinary way, these jerky displacements of the eye cause a successive series of discrete pictures of the star to be formed on various points of the retina, each picture being made with an exposure time of the order of 0·1 second. Thus, if we look at a star for a minute or so, hundreds of successive, discrete light images of the star can be formed on the retina. But, of all these, only a few may have reached the threshold of stimulation of the retina. And, by prolonging the time of observation, the chance of having at least one successful exposure increases. Accordingly, dimmer stars may be seen when the time of observation is increased, this effect occurring purely on the grounds of probability, without any temporal summation of the retinal effect of light over such protracted periods—which are much longer than the retinal action time.

Among other things, these considerations show that, in order to determine the minimum energy necessary for the stimulation of the retina, special control of at least the temporal and spatial factors must be achieved. This is obviously necessary if it is desired to interpret the results in terms of quantum fluctuations. Every source of variation, which can be removed, must be removed from the experimental conditions.

In particular, continuous sources of light must not be used. Brief flashes of light must be presented to the subject of the experiment. The duration of the flashes must be shorter than the retinal action time. The method of fixation and flash outlined at the beginning of this paper must be used.

Measurement of the Minimum Energy necessary for Vision

It may be advisable to describe briefly the new determination made recently by Hecht, Shlaer and Pirenne [11] of the smallest amount of energy necessary for a visual response. Only the essentials can be given here and the reader must be referred to the original paper for details on a number of points.

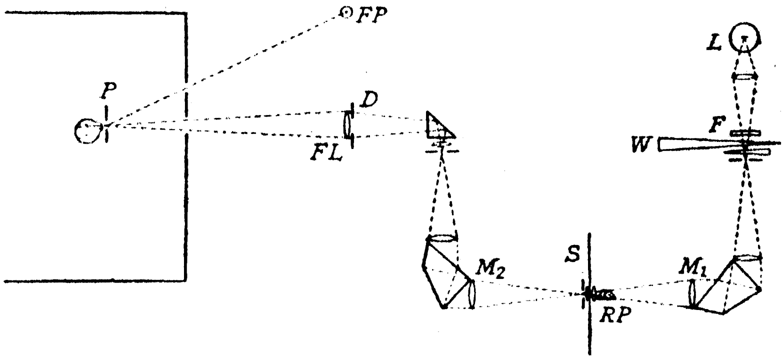

Fig. 1.—Optical system for measuring minimum energies necessary for vision.

The eye at the pupil P fixates the red point FP and observes the test field formed by the lens FL and the diaphragm D. The light for this field comes from the lamp L through the neutral filter F and wedge W, through the double monochromator M_1M_2 and is controlled by the shutter S.

(*From* Hecht, Shlaer *and* Pirenne [11].)

Fig. 1 gives a diagram of the apparatus. The light source is a ribbon filament lamp L run on a constant current. By means of a lens the light is focused on the slit of a double monochromator M_1M_2 and finally falls on to the artificial pupil P. The artificial pupil is a circular hole, 2 mm. in diameter, drilled in a metal plate. As this aperture is smaller than the pupil of the eye, the variations in the size of the latter need not be taken into account in the measurements.

The subject of the experiment sits in a dark room containing the apparatus. His head is kept in a fixed position in the following way. An impression of his upper jaw is taken in hard wax before the experiment and rigidly attached to the apparatus. When he sits for the experiment, he takes the dental impression between his teeth. His left eye is then next to the artificial pupil P. The subject looks through P at the fixation point FP which is a dim point source of red light. He may then see laterally the lens FL filled with light. This lens, suitably diaphragmed, constitutes the test field.

Thus the position of the head is fixed by the use of the dental impression, and the position of the eye in its orbit is fixed and is the same each time the subject directs his gaze at the fixation point.

In this way we succeed in keeping the retina in a definite, reproducible position while we make a certain amount of light strike a specified region of it—the optical image of the test field.

Using such an arrangement, the lens *FL* is seen by the subject as a uniformly illuminated field. The light intensity can be varied by using neutral filters *F* and the neutral wedge *W*. The exposure time is fixed by the precision shutter *S*, which allows the light to pass for one-thousandth of a second when the subject releases a key.

Energy calibrations are made essentially by replacing the eye by a thermopile, the light intensity being made as high as possible by removing the neutral wedge, etc.; the artificial pupil being also removed. The same thermopile is afterwards subjected to the radiation of a standard lamp emitting a known amount of radiant energy and the galvanometer deflections in the two cases are compared. On this basis, a straightforward calculation gives the amount of energy passing through the artificial pupil, and striking the eye, in the experiments.

From the point of view of the subject, the result of all these arrangements is fairly simple. In the surrounding darkness the subject sees nothing but the red fixation point *FP* (Fig. 2). When,

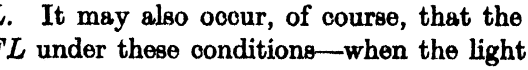

Fig. 2.

having fixed his gaze on *FP*, he releases the shutter key, he sees for an instant "with the corner of his eye" a small patch of light, the test field *FL*. It may also occur, of course, that the subject sees nothing at *FL* under these conditions—when the light intensity in the test field is too low. In any case, the experimenter knows in each trial the (nominal) amount of light energy which, coming from the test field, has struck the cornea of the subject. As will be seen, a complete experiment involves the presentation of several hundred flashes of various nominal energy contents. While it might perhaps be thought that it should be easy for the subject to say whether or not he has seen the test field, in fact it is not so, and a considerable amount of concentration is required.

In order to reach the smallest possible value of the light energy necessary for a visual response, the following physiological conditions were chosen:

(1) Complete dark adaptation of the eye. The subject waited three-quarters of an hour in the dark before the experiments were begun.

(2) Light of wavelength $\lambda = 0{\cdot}510\ \mu$, to which the retinal rods are most sensitive, was used.

(3) The angle-(fixation point)-eye-(test field) was 20°. Under these conditions, the image of the test field fell into a peripheral region of the retina, containing many rods, 20° from the fovea.

(4) The circular test field, defined by the diaphragm *D* in front of the lens *FL*, had a diameter subtending an angle of 10′ of arc at the eye.

(5) The flash of light illuminating the test field lasted for 0·001 second.

Only trained and reliable observers were used as subjects in the experiments. Very special precautions were taken from the psychological point of view. These psychological conditions cannot be described here, but most of them are really a matter of common sense. They aimed at preventing fatigue in the subject, and at bringing him back to the highest possible state of attention each time a flash was presented to his eye.

For seven subjects, the minimum amounts of energy necessary for vision have thus been found to range between

$$2{\cdot}1 \text{ and } 5{\cdot}7 \times 10^{-10} \text{ erg.}$$

Referring to the above-given value of the quantum for the wavelength $\lambda = 0{\cdot}510\ \mu$, this corresponds to numbers ranging between 54 and 148 quanta. These quantities represent the nominal energy content of a single flash striking the cornea, under conditions where 60 per cent. of the flashes are seen—and 40 per cent. are not seen—by the subject.

The minimum amount of energy necessary for vision must be defined in such a statistical manner because, even in the best-controlled experiments, there is never a sudden jump from a nominal intensity at which the light is never seen to a nominal intensity at which it is always seen. On the contrary, there is a smooth transition from one to the other as the setting of the wedge is progressively changed to make the light more and more intense. For any nominal intensity in this region of transition, the light is sometimes seen, and sometimes not seen. The region of transition has a considerable extent, far beyond any experimental error. The intensity must be increased by about a factor 10 to pass from conditions where the light is practically never seen to conditions where it is almost always seen. This is the experimental variability of response which will be discussed presently in connection with the theory of quantum fluctuations.

Action of the Light on the Retina in these Experiments

In order to find what is the physical stimulus acting directly upon the organism, we must determine the fraction of the above amounts of light which is absorbed by the retina. The losses of light which occur by reflection at the cornea and by absorption in the optical media must first be taken into account. They are of the order of 50 per cent. In what concerns the rod layer in the retina, it is very likely that not more than 20 per cent. of the light which reaches it is absorbed by it, 80 per cent. passing through and being lost. This value has been obtained in two different ways which agree reasonably well. A direct estimate has been made on the basis of the data of investigators who extracted visual purple from the retina of rats, rabbits and, in one case, of man. An indirect estimate was obtained by comparing the shape of the visibility curve of the dark-adapted eye with the shape of the spectral absorption curve of visual purple at different concentrations. The reader must be referred to the original paper [11] for details of these calculations, which are of crucial importance, but which, from the nature of the case, cannot be expected to have perfect accuracy, since all eyes cannot be assumed to be identical in this respect. It appears, however, that the value of 20 per cent. absorption is probably an upper limit. Using it, we find that at the threshold the nominal number of quanta absorbed by the visual purple in the rods is only 5 to 14 quanta.

We must see now how these quanta act upon the retina. The image of a test field whose diameter subtends an angle of 10′ at the eye, covers on the retina an area containing about 500 rods. Each of the 5 to 14 quanta thus absorbed in the given retinal area has about the same chance of being absorbed in any one rod. It may therefore happen that several quanta are absorbed in the same rod. It might therefore be suggested as a possibility that a stimulation sufficiently strong for the light to be seen is produced in the optic nerve only when at least two quanta are absorbed in one and the same rod. But this suggestion must be rejected, for the following reason: in terms of the total number of rods available and of the number of quanta involved, it is an easy matter to calculate the probability of having two quanta absorbed together in any one of the rods. The probability will be very small, much less than 60 per cent., in fact, which is the frequency with which the light is seen in the experiment. It appears therefore that such a "double hit" cannot be a necessary condition of an adequate stimulation. Furthermore, by reducing the size of the test field, the number of rods involved is decreased. This in turn increases the probability of

a double hit. Yet the threshold energy for smaller fields is not less, but rather more than that for the 10′ field. This appears to rule out the possibility that a double hit be the condition for stimulation.

Thus the light is seen when each of the 5 to 14 quanta is absorbed in a different one of the 500 rods covered by the image of the test field.

We are therefore led to enquire about the effect produced in a single rod by the absorption of one single quantum. According to the photo-equivalence law of Einstein, when light acts upon a chemical substance, for instance, when it bleaches visual purple, the initial process consists in the absorption of light, in quanta, by the individual molecules of the substance. One may therefore state that, when one quantum is absorbed in one retinal rod, only one molecule of visual purple is affected in the initial stage. But this single molecule, thus transformed by light, may be able to start a series of physico-chemical reactions involving other molecules, and leading eventually to some form of nervous stimulation. As a reactive system, a retinal rod thus reaches the absolute limit of sensitivity set by the quantum and molecular theories.

Anatomical studies show that in the vertebrate retina, many rods converge through a nervous relay station on to one single fibre of the optic nerve [12]. Electro-physiological experiments also show that one nerve fibre has in the retina an extended receptive field, inside which summation of the effects of light can occur [13]. It may be concluded, therefore, that when a number of rod cells has been stimulated, each by the absorption of a single quantum, a summation of their individual stimulations takes place at the level of the nervous relay station. The stimulation can then spread to other parts of the nervous system, and the organism responds to the flash of light.

The events which take place in the threshold experiments may therefore be tentatively imagined as follows : In each of a number of rods among the group of 500, one quantum is absorbed by one molecule of visual purple. In each of these rods this molecule starts reactions leading to the stimulation of the nervous structure of the rod cell. A single stimulation of this kind is not capable of itself of overcoming the barrier on the way to the higher nerve centres. However, a summation of the individual stimulations occurs at the level of the relay cell to which the rods are connected. When the number of rods simultaneously stimulated is large enough the stimulation of the relay cell is propagated by an optic nerve fibre to higher nerve centres, so that eventually the subject signals that he has seen the light.

The lowest possible state of activity which can be produced in the optic nerve is the discharge in one single impulse by one single fibre. It is not known whether the threshold stimulation discussed here corresponds to this very minimum, or to a greater state of nervous activity. But, for any given biological state of the organism, this nervous stimulation which will make the subject signal "seen" must, whatever it is, have a certain definite value.

Quantum Fluctuations

When a sufficient stimulation is produced in the optic nerve, the subject signals that he has seen the light. In order to produce such a nervous stimulation, a given number n of quanta absorbed by the retina are, in turn, needed. This retinal threshold n has been estimated above as ranging in different subjects between 5 and 14 quanta. When n or more quanta are absorbed, therefore, the organism gives a response. When less than n quanta are absorbed, there is no response. The threshold n may vary from trial to trial, even in the course of the same experiment; but it must have a definite value for each particular trial.

Let us assume now that in all the trials made in a given experiment with a given subject this retinal threshold n is constant, and is for instance $n = 6$. It has been said already that, on the basis of quantum theory, it is not possible to set up conditions such that for each flash the retina would absorb a constant number of quanta, say 6. (And it would be quite impossible to arrange for a constant number of quanta to be absorbed by any purely physical apparatus instead of the retina.) In order to demonstrate this in a particular case, let us assume that in a series of flashes a number of 30 quanta each time reaches the layer of rods in the retina, and that the visual purple in this layer absorbs 20 per cent. of the light incident upon it. Absorption of light occurs by independent quantum processes. In each of these processes, one of two things must happen: either the quantum is absorbed, or it is not. An absorption of 20 per cent. simply means that each quantum has 20 chances in 100 of being caught by one of the molecules of visual purple, and 80 chances of passing through the layer and escaping free. It is true that on the average a number, equal to $30 \times 0{\cdot}20 = 6$ quanta, will be absorbed by the rods, while the remaining 24 quanta will come through. The value 6, however, represents simply the mean of the numbers actually absorbed in a large number of trials. To take an extreme case, it might happen by chance that all 30 quanta got through the rods, none being absorbed by them. Since each of the quanta has a probability equal to 4/5 of not being absorbed, and these proba-

bilities are independent of one another, the probability of all 30 quanta passing through is obtained simply by taking the product of all the probabilities relating to each quantum separately. This product is $(4/5)^{30}$; this is a small, but finite number. It is also possible, but improbable, that all 30 might be absorbed ; the probability here is $(1/5)^{30}$. The actual number of quanta absorbed, in other words, may vary each time. It may have any value between 0 and 30 and the probability of occurrence of each value can be calculated.

This is enough to show that the number of quanta exciting the retina is bound to vary even when all conditions are kept rigorously constant. It can be shown on similar grounds that it is also impossible to set up a source of light emitting a constant number of quanta in a constant period of time. It is therefore impossible to cause a constant number of 30 quanta to reach the retina in each trial, as assumed in the above argument. But this only emphasises still more the variability of the number of quanta absorbed by the retina, which this argument was precisely designed to demonstrate.

Referring again to the simile of the slot machine, such a variability would mean there that it would be impossible to insert always exactly 6 pennies in the slot. Sometimes the number inserted would be 6, sometimes 7 or more, sometimes 5 or less, sometimes even 0.

There is no way of restraining quantum fluctuations. If a large number of quanta is involved in emission or absorption, the variability of this number on a percentage basis will be less than in the case of a smaller number of quanta. This follows from pure considerations of probability. A powerful source of light emits very large numbers of quanta : the number of quanta emitted in unit time, that is, the intensity of the source, can therefore have a very high degree of constancy on a percentage basis. The use of an intense light source, however, would be of no avail in attempts to deliver constant small numbers of quanta to the retina, because the intensity would have to be cut down by absorbing a large proportion of the light on its way to the eye ; the variability would then reappear for the same reasons as were given above.

In fact the variability, under constant experimental conditions, of the number of quanta absorbed by the retina depends only upon the average or nominal number of quanta absorbed. It does not depend on what occurs to the light before it is absorbed. Moreover, for any given nominal number—which being an average can be fractional—the actual number may be 0, or 1, or 2, or 3, or any other integer. There is no upper limit to the value of this number. Actual numbers of quanta much higher than the average number are

not impossible because, among other reasons, the source of light may suddenly emit by chance many more quanta than the average. On the other hand, it is always possible that the actual number may be zero, because as has been seen, the quanta reaching the retina may by chance all fail to be absorbed. The more the actual number differs from the average number, the less likely it is to occur, however. Absorption of numbers of quanta much larger than the average is highly improbable.

Frequency-of-Seeing Curves

For any value of the nominal average number of quanta absorbed by the retina, the actual number fluctuates, being any integer from zero upwards. A formula, derived by the mathematician Poisson, applies in the present case and gives, in terms of the nominal number a alone, the probability that the actual number will be any number x chosen for consideration. This probability is equal to $a^x/e^a x!$. When the nominal number a is 6, for instance, the probability that the actual number x will be 0, 1, 2, 3, 4, or 5, is at once obtained using the Poisson formula. The probability of $x = 0$ is found to be 0·002; that of $x = 1$ is 0·015; that of $x = 2$ is 0·045; that of $x = 3$ is 0·089; that of $x = 4$ is 0·134; that of $x = 5$ is 0·161. The sum of these various probabilities, 0·446, is the probability of the actual number being less than 6. If this composite probability is then subtracted from unity, the result, of course, is the probability that the actual number x will be 6 or more, when the nominal number is 6. This probability is $(1 - 0{\cdot}446) = 0{\cdot}554$. Thus if the retinal threshold n of the subject is constantly equal to 6 and if constant conditions, chosen so that the retina absorbs on the average a number $a = 6$ quanta, are maintained, the subject will see the light in about 55 per cent. of the trials and he will fail to see it in about 45 per cent.—even though his threshold n, or his sensitivity to light, is assumed to be invariable.

For any other value of the nominal number, the probability of 6 quanta or more being absorbed can be calculated in the same way. When these probability values are plotted against the corresponding nominal numbers, a curve is obtained showing how the probability of seeing the light must vary with the light intensity. The curve marked 6 in Fig. 3 has been calculated in this way. Its ordinate is the probability of 6 or more quanta being absorbed; its abscissa is the logarithm of the nominal number of quanta absorbed. (The logarithmic scale is used for reasons which will be apparent later.) For the nominal numbers smaller than 1·5 (1·5 corresponding to 0·18 on the abscissa scale in log units), the probability is almost

zero. As the nominal number increases above this value, the probability increases rapidly, reaching almost to unity (or 100 per cent.) for a nominal number equal to 15 (corresponding to 1·18 on the abscissa scale).

In calculating the curve just considered it was assumed all through that the retinal threshold was $n = 6$. Similar curves corresponding to different values of n can again be calculated in the same way. They are given in Fig. 3 for n varying from 1 to 9. As the number n increases the curve is displaced as a whole towards

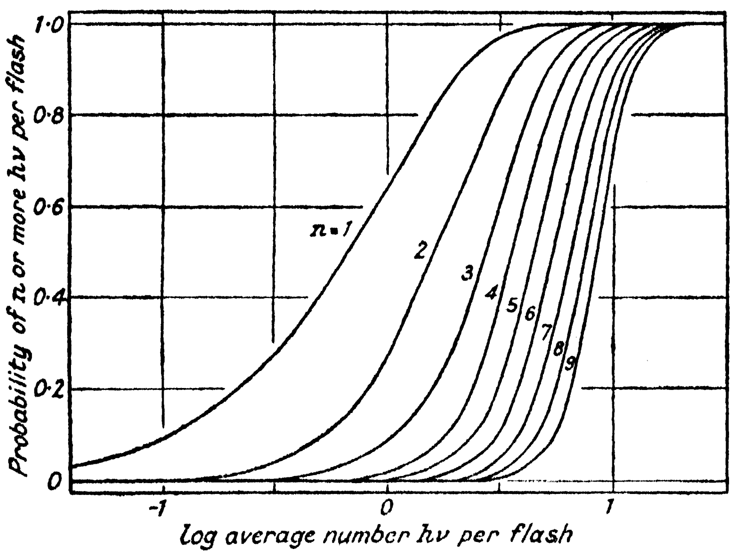

FIG. 3.—Poisson probability distributions.

For any average number of quanta ($h\nu$) per flash, the ordinates give the probabilities that the flash will deliver to the retina n or more quanta, depending on the value assumed for n.

(*From* HECHT, SHLAER *and* PIRENNE [11].)

higher abscissæ values. The intermediate S-shaped region of the curve also becomes steeper. (If there were no quantum fluctuations these S-shaped curves of course would each be replaced by vertical lines at the particular value of the abscissa corresponding to the retinal threshold, the probability of seeing jumping from zero to unity along this line.)

Now for a given subject, at one sitting, it is possible to determine experimentally, point by point, the curves giving the frequency with which the light is seen in terms of the intensity of the flash. These curves—which have been mentioned in the paragraph on experimental measurements—can then be compared with the theoretical curves of Fig. 3.

In order to do so only the nominal number of quanta striking the cornea in the trial, not the nominal number a absorbed by the retina, need be known. The frequency curves are plotted against the logarithm of the flash intensity and their shape is compared with the shape of the theoretical curves. The shape of the curves is then independent of the intensity units used because of the use of this logarithmic scale. (For, when intensity units are changed, all intensity values are multiplied by a constant factor. Such a multiplication is equivalent to the addition of a constant quantity to the values on a logarithmic scale. This merely shifts the curves bodily along the scale.) An independent estimate of the value of the retinal threshold n can therefore be obtained by such a comparison.

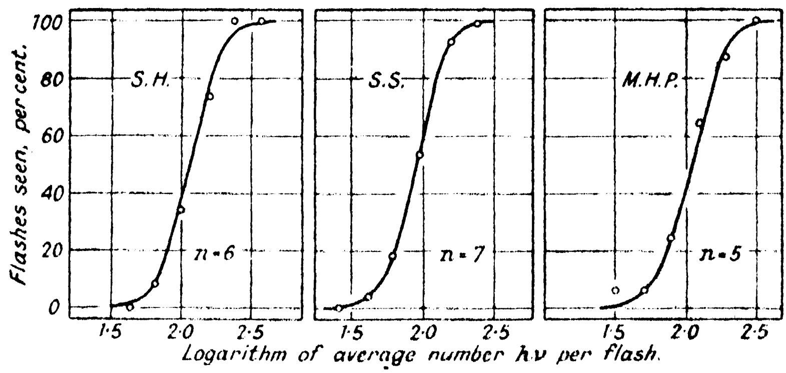

FIG. 4.—Relation between the average energy content of a flash of light (in number of $h\nu$) and the frequency with which it is seen by three observers.

Each point represents 50 flashes. The curves are the Poisson distributions of Fig. 3 for n values of 5, 6 and 7.

(*From* HECHT, SHLAER *and* PIRENNE [11].)

In Fig. 4 the frequency-of-seeing curves obtained with three different subjects are compared with curves calculated on the basis of purely physical fluctuations, as has just been explained. The circles represent the measurements, and the continuous line the probability curves calculated for retinal thresholds of $n = 6$, $n = 7$, and $n = 5$ respectively. The shape of these particular theoretical curves agrees well with that of the experimental curves.

If the retinal threshold n was constant in each of the experiments, as assumed in the calculation of the curves, it may then be concluded that n has respectively the values 6, 7 and 5 for the three different subjects. This is in good agreement with the direct determination of n, which gave values ranging from 5 to 14 quanta.

Suppose the frequency-of-seeing curve of a particular subject

has a shape corresponding to $n = 6$. Suppose, secondly, that it could be accurately established by the direct method that in the same experiment the average number of quanta absorbed by the retina at the threshold was also equal to 6. It would then be definitely proved that the retinal threshold n was constant and equal to 6 in this experiment, and that the uncertainty of seeing the light was entirely due to physical fluctuations. The direct determination of the number of quanta absorbed by a living retina is, however, complicated by unavoidable uncertainties. It cannot therefore be established with certainty whether or not n remains constant during one of these experiments, and whether or not the physical fluctuations are the sole cause of the observed frequency-of-seeing curves. The accuracy of the data, however, is sufficient to prove that the physical fluctuations are of very considerable magnitude and play a major rôle in the experiments.

It may be worth pointing out that constancy of the retinal threshold n does not imply perfect constancy of the organism, for n cannot vary by less than unity. If n, for instance, changes from 6 to 5 or from 6 to 7, these are variations of more than 15 per cent. If a numerical value may be ascribed to the sensitivity of the nervous mechanism connected to the retina, this sensitivity might therefore vary by, say, $\pm$ 15 per cent. without bringing about a change in the value of n. The analogy of the slot machine responding to a certain number of pennies may make this clear. Concerning the way in which biological variations of n should be taken into account in the calculations the reader is referred to the original paper [11].

As was said at the beginning of this paper, in the past it was generally assumed that, when an organism gave a variable response to a physical stimulus, the variability must be due to the organism, while the stimulus was taken to be constant. The present results, on the other hand, show that in the case discussed the organism may possibly be constant while the physical stimulus certainly undergoes wide and unavoidable fluctuations.

Fluctuation phenomena are very important throughout modern physics. They are observed in the case of electrons, α-particles, molecules, as well as quanta. On account of the very high sensitivity of the eye, it is therefore not surprising that one should find quantum fluctuations operative in its behaviour in certain circumstances. The study of these fluctuations opens a promising new field in the physiology of vision [14].

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A SHORT HISTORY OF THE TASMAN GEOSYNCLINE OF EASTERN AUSTRALIA

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Introduction

THROUGH much of geological time many parts of the area now occupied by Australia and the adjacent lands and seas were covered by basins of deposition both marine and terrestrial. Passing over the Early and Middle pre-Cambrian sedimentation, the conditions of which are by no means clear, we find evidences of an Upper pre-Cambrian marine trough running north from Kangaroo Island and the Mt. Lofty Ranges in South Australia and turning sharply west through the Macdonnell Ranges in Central Australia; later this trough expanded into a great shallow depression that covered Northern Territory, much of Western Australia and South Australia, and part of western Queensland and New South Wales. It may have persisted into the Palæozoic Era, but by the end of Cambrian time most of it had become land as the result of widespread diastrophism. Another depression, called by Teichert the Westralian geosyncline, which bordered Western Australia irregularly in the north and west, seems to have come into being in Devonian and to have persisted till Pliocene time. During most of the Palæozoic Era a great part of eastern Australia was occupied by the Tasman geosyncline, and in Lower Cretaceous time a wide epeiric sea, developing from the vast Jurassic Lake Walloon, traversed the continent from the Gulf of Carpentaria to the Great Australian Bight. Finally, there is some evidence that a great curving trough, which may be called the Papuan geosyncline, stretched from the Dutch East Indies and New Guinea through New Caledonia to New Zealand. Though doubtless in existence much earlier, it seems to have been best defined in Mesozoic and Tertiary times; probably it was in communication with Tethys through the Malay Peninsula and Burma, and to it were linked the Australian geosynclines and epeiric seas.

Of all these basins of deposition the greatest was the Tasman geosyncline. The reconstructions of it given by Walkom (1913, 1918), Jensen (1912), Benson (1923), Bryan (1926), Bryan and Whitehouse (1926), Andrews (1938), and others display a wide diversity of interpretation, but this arises naturally from the fact

that the fewer the data the greater the number of degrees of freedom available to the would-be interpreter. Though many matters are still obscure and much stratigraphical and structural detail is lacking, it is felt that the information now in hand is sufficient to enable an outline of the history of the geosyncline to be sketched and its varying boundaries to be roughly indicated; nevertheless, the present account is to be looked upon as but one more interpretation. One great difficulty in the way of satisfactory reconstruction is the fact that over large areas in western Queensland and New South Wales and in northern Victoria the Palæozoic strata are buried beneath Mesozoic and Cainozoic deposits, and another results from the extensive removal of strata by erosion that has taken place at intervals throughout geological time.

It was formerly held that eastern Australia was built up to the east and north-east of a pre-Cambrian nucleus or shield through deposition in a one-sided trough on the continental shelf, which was periodically subject to the influence of forces acting from the Pacific; as a result its sediments were folded and elevated and added to the increasing total of continental land, while at the same time the axis of sedimentation migrated to the east and north-east. In 1916 the late Prof. Schuchert named the trough the Tasman geosyncline and, influenced no doubt by the concept of a former easterly extension of the Australian continent put forward by Marshall (1912) and others, depicted it as bounded on the west by Australia, and on the east by an unnamed land stretching across what is now the Tasman Sea. Schuchert's interpretation was adopted by Walkom (1918) and implicitly by Sussmilch and David (1919), who named the lost land *Tasmantis*, and is now accepted by most if not all Australian geologists. The general trend of the trough is indicated by the remarkable though not invariable constancy in the direction of the axes of folding, which in Tasmania, Victoria and New South Wales are broadly submeridional and in Queensland on the whole north-north-west. In some reconstructions the trough has been represented as closed to the north, but in view of the many striking faunal affinities of its sediments with those of Europe, Asia and North America we cannot but believe that its chief communications with the rest of the world were to the north during most of its life.

Cambrian Period

The beginnings of the geosyncline are involved in some obscurity. Its earliest known deposits are unfossiliferous, but are probably Cambrian; they comprise the Greenstone series at the base of the

formation known as the Brisbane Schists in south-eastern Queensland, and the cherts, tuffs, etc., constituting the Wagonga series * on the far South Coast of New South Wales. In default of better evidence the Cambrian geosyncline may be depicted as in Fig. 1, p. 630, but probably it extended much farther to the west. The fossiliferous Cambrian rocks of Victoria and Tasmania were probably laid down in it.

The tectonic history of these Cambrian rocks is not definitely known. In Tasmania there is evidence of a marked orogeny of probable Upper Cambrian age, but this disappears to the north, and in Victoria Middle and Upper Cambrian and Lower Ordovician strata are conformable. The Wagonga Series, unconformably overlain by Upper Ordovician graptolitic shales, may have shared in the Upper Cambrian diastrophism, but the Greenstone series of Queensland is perfectly concordant with the Ordovician (?) Bunya phyllites, and was not deformed till late Silurian time. Possibly the strata of the geosyncline were folded during the Cambrian orogeny along parallel but impersistent belts between which deposition was uninterrupted. So far as is known no magmatic injection was associated with the folding.

Ordovician Period

Though outcrops of fossiliferous Ordovician rocks are not widespread there are some reasons for thinking that the Ordovician geosyncline may have been approximately as represented in Fig 2, p. 630. Lower Ordovician graptolitic sediments are well developed in central-western and sparsely in eastern Victoria, but disappear to the north under Cainozoic deposits and are known at only one spot in western New South Wales. Upper Ordovician rocks are widely distributed in central and eastern Victoria and in the eastern highlands and South Coast belt of New South Wales, where they comprise carbonaceous shales and slates, with phyllites, tuffaceous sandstones and a very little limestone. Slates and phyllites apparently devoid of fossils but almost certainly Lower and Upper Ordovician appear in north-eastern New South Wales and as part of the Brisbane Schist formation, and there are phyllitic rocks, some demonstrably pre-Silurian, in central and northern Queensland, which are also probably Ordovician.

The full Ordovician sequence may be present in Tasmania, but our knowledge of it is very incomplete. At and near the base, and

* Name suggested by Dr. Ida A. Brown, who has investigated them.

possibly descending to the Upper Cambrian, are limestones, sandstones and conglomerates with a shallow-water fauna. Limestones also appear near the top.

In Central Australia, chiefly south and north-east of the Macdonnell Ranges, are Ordovician sandstones and shales folded along east–west axes and resting unconformably on Lower Cambrian beds. They enclose a shallow-water or littoral fauna similar in some respects to that of the Tasmanian beds but much younger. Whether the Amadeus Trough, in which they were laid down, was in direct communication with the Tasman geosyncline we are unable to say definitely.

The Ordovician Period was closed by what may be called the *Benambran* orogeny, during which a median geánticline some 200 miles wide was formed traversing eastern Victoria and the eastern highlands of New South Wales. Its width, where to the north it disappears under the Mesozoic beds of the Great Artesian Basin, is sufficient indication of a considerable extension into Queensland, and it may have continued as shown in Fig. 2, p. 630. Along this belt wherever they are seen in contact the Ordovician and Silurian rocks are unconformable, but on either side of it, in Tasmania and central-eastern Victoria, and in the north-east of New South Wales and the south-east of Queensland, there is perfect angular conformity.

With the Benambran folding came the injection of synchronous bathyliths. The known intrusions form two parallel belts, one of which begins in eastern Victoria, attains its maximum development in the Bogong and Benambra highlands, and has been traced in New South Wales at intervals in a N.N.W. direction for about 200 miles. The other belt, 50 miles to the east and very much shorter and narrower, passes north through Cooma (N.S.W.) into the Australian Capital Territory: here the slates and sandstones, which through folding or deep burial had acquired low-grade metamorphism, suffered contact-alteration which reached its maximum intensity, with the crystallisation of sillimanite and the formation of a zone of granitisation and *lit-par-lit* injection. The granites are everywhere much contaminated and locally take on the appearance of banded gneisses.

Silurian Period

Through erosion of the Benambran geanticline and its gradual submergence the two flanking or sequent geosynclines of early Silurian time eventually coalesced, so that by the end of the Lower Silurian epoch almost the whole of the tectonic ridge was again

beneath the sea. Ultimately the Silurian geosyncline had much the same extent as the Ordovician except that its western margin, in Victoria at least, had shifted 100 miles to the east, possibly as the result of late Ordovician vertical uplift (Fig. 3, p. 630). Apart from the abundance of muddy sediments the geosyncline was remarkable for its great development of coral-reefs, which stretched at intervals for more than 1800 miles from northern Queensland to south-western Tasmania and over a width of 200 miles. Farther east the water was possibly too deep for reefs to form.

No great tectonic movements occurred in the Silurian Period, but at its close a major orogeny affected the whole of the geosyncline except for a narrow western strip in the lee of the Benambran geanticline (Fig. 3, p. 630), of whose sediments remnants survive in central-eastern Victoria and possibly in Tasmania. This *Bowning* orogeny varied in intensity from place to place and was on the whole most severe in the east. In south-eastern Queensland, and perhaps also in Victoria, Cambrian and Ordovician beds shared in the deformation.

The boundary of the Silurian geosyncline in Queensland is, of course, conjectural for, apart from the fossiliferous limestones of Chillagoe in the north and the probable Silurian Neranleigh and Fernvale series in the south-east, no rocks of this age are known in the state. But the width of the folded belt in New South Wales, stretching as it does from Cobar across to the coast, makes it clear that there must have been a considerable northerly extension of the geosyncline.

The Bowning folding was accompanied by igneous injection, and bathyliths and lenses of granite and quartz-diorite with primary and cataclastic foliation are found in several places in New South Wales and eastern Victoria, some of them associated with schistose porphyry and porphyrite. This was, apparently, the last occasion during the life of the geosyncline when the intrusions related to an orogeny were of the synchronous type. Like those of the Benambran epoch the Bowning intrusions are by no means so numerous as one might expect in view of the large area subjected to folding.

Mystery surrounds the deposition of the unfossiliferous thick Pertnjara conglomerates of the Macdonnell Ranges, Central Australia. Resting directly on the Ordovician beds, with which they are folded along east–west axes, they are, as Andrews has pointed out, most reasonably to be regarded as Silurian, and with their deformation, probably during the Bowning epoch, deposition in the Amadeus Trough came to an end. Whether or not the basin of their deposition was directly connected with the Tasman geosyncline we cannot say.

Devonian Period

Following the Bowning orogeny all that remained of the geosyncline at the beginning of Devonian time was a western channel, perhaps not more than 100 miles wide, extending north, in all probability, into New South Wales and Queensland and south into Tasmania, where there are some indications that, as in Victoria, Upper Silurian pass up into Lower Devonian beds. The sea, however, soon began to spread east again across the denuded and sinking geanticline, and by the end of Middle Devonian time had passed beyond the present coast-line (Fig. 4, p. 630). During these epochs coral-reefs were abundant from a little south of Townsville (N. Queensland) to Victoria and possibly even to Tasmania. In the deeper waters radiolaria abounded and volcanic activity was considerable.

An end was put to Middle Devonian deposition by the *Tabberabberan* orogeny. Since the folded beds suffered extensive erosion before Upper Devonian sedimentation began, the limits of the folded belt are rather hard to determine. Deformation was very marked in central and eastern Victoria, and is traceable north through New South Wales as far as the edge of the Great Artesian Basin. The conformity of Middle and Upper Devonian beds in the North Coast area of New South Wales and in eastern Queensland fixes an approximate eastern limit to the geanticline. An indirect approach to the determination of the former extent of the geosyncline and the position of its western boundary is based on the following reasoning :

(*a*) The existence of bathyliths and stocks of granite and allied rocks in any area implies the former deposition there of geosynclinal sediments, in connection with whose folding the magma was injected (quite often, of course, we now find the granite in contact only with the basement-rocks of the geosyncline, the strata involved in the orogeny having been eroded away) ;

(*b*) The known late Ordovician and late Silurian bathyliths are of synchronous type and their granites are more or less gneissic ; all the known later intrusions are of massive granite : thus a massive granite intrusive into Ordovician or Silurian and overlain by Upper Devonian strata may fairly be regarded as Tabberabberan.

By applying these criteria, though their validity is admittedly by no means unimpeachable, it is possible to deduce that the Middle Devonian geosyncline extended and its strata were folded to at least as far west as Cobar in New South Wales and to about the same longitude in Victoria ; the prolongation of the geanticline into Queensland is of course an extrapolation. Of Tasmania we know

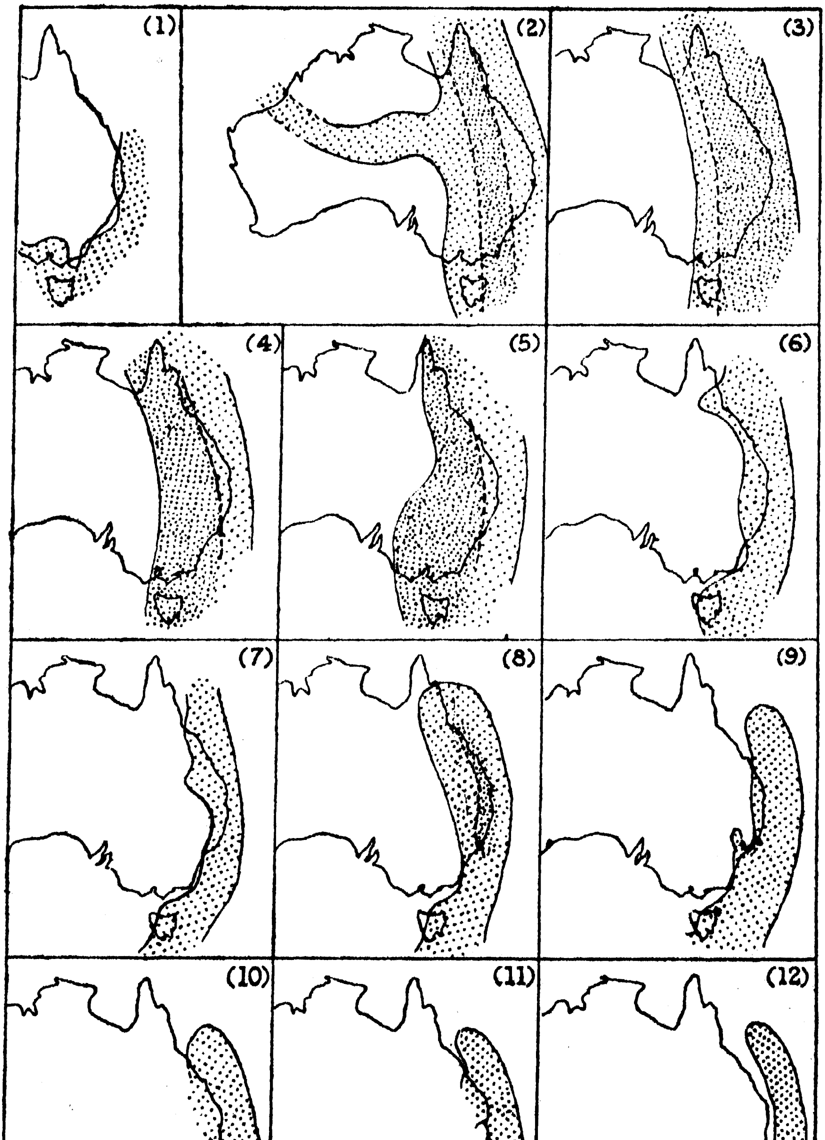
very little indeed, but on palæogeographical grounds it is hard to escape the conclusion that the island was in the geanticlinal belt, and possibly here, as in central Victoria, Ordovician and Silurian beds were involved in the folding, as the result of which the locus of deposition was pushed far to the east. Though igneous activity was associated with the orogeny and a number of intrusions are reasonably assigned to it, only a few in Victoria and New South Wales can be definitely dated ; they are chiefly granites and granodiorites, porphyries and porphyrites, and include those responsible for introducing the gold and copper ores in the Cobar-Nymagee-Mt. Hope area in western New South Wales, and possibly certain porphyrites which are thought to be related to gold and copper deposits in western Tasmania.

After an interval of erosion the Upper Devonian epoch witnessed a remarkable westward expansion of the geosyncline, which in New South Wales and probably also in Victoria almost reached the South Australian border (Fig. 5, p. 630). In both Queensland and New South Wales the sediments were marine and of muddy facies in the east, but paralic—mostly sandstones and red shales—in the west, and in Victoria they seem to have been almost entirely lacustrine. Indeed, the geosynclinal character of the depression might be called in question but for the fact that the paralic and lacustrine beds have been folded and invaded by bathyliths.

It has been held by some New South Wales geologists that this folding occurred at the close of Devonian time, but field-observations show that in Queensland, New South Wales and Victoria wherever fossiliferous Upper Devonian of either facies are in contact with Lower Carboniferous beds relations are perfectly conformable, and indeed that owing to lithological similarities it is often hard to make a precise separation of them. It is far more probable that Upper Devonian and Lower Carboniferous beds were folded together about the end of Viséan time, as argued below.

Carboniferous Period

The early Carboniferous was thus probably co-extensive with the late Devonian geosyncline. The Lower Carboniferous strata in Queensland are marine in the east and lacustrine farther west, but any possible transition between the two facies is hidden beneath later deposits. In New South Wales the lowest Carboniferous beds, confined to the eastern part of the state, are marine, fossiliferous, and approximately equivalent to the Tournaisian of Europe ; in part they pass up into Viséan marine beds, but along a narrow strip where slight uplift caused an easterly retreat of the sea they are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overlain by lacustrine beds and terrestrial volcanic deposits with occasional small marine intercalations. The Lower Carboniferous rocks of Victoria are entirely terrestrial with the possible exception of the Grampian sandstones in the far west, which have a small marine fauna either Upper Devonian or Lower Carboniferous.

A Lower Carboniferous orogeny was determined for Queensland by Reid, and is inferred also for New South Wales, where in the Lower Hunter valley an unconformable junction has been noted between terrestrial Lower Carboniferous (= Viséan) beds and an Upper Carboniferous series. Elsewhere this same series begins with a heavy conglomerate which rests conformably or with slight angular unconformity, and with a marked lithological break, on the Lower Carboniferous beds. In addition, there is in several places violent unconformity between Permian and Upper Devonian or Lower Carboniferous beds, whereas later Carboniferous and Permian beds when occurring in the same sequence are invariably conformable.

Reid referred to the Queensland orogeny as the Drummond movement, but the name of *Kanimblan* given by Sussmilch to that which folded the Upper Devonian rocks in New South Wales has priority, though he was uncertain as to its precise date, which must have been close to the end of Viséan time.

In Victoria the Lower Carboniferous beds are nowhere known in contact with the later Carboniferous tillites, but the latter pass up into Permian beds with *Gangamopteris*.

The Kanimblan orogeny was probably the greatest in the history of the Tasman geosyncline. The folded area must have comprised practically the whole extent of the geosyncline from the extreme north of Queensland to the extreme south of Tasmania except for a relatively narrow strip in eastern Queensland and New South Wales, where the Carboniferous sequence is unbroken. The later isostatic or tensional phases of the movement were marked by a wonderful display of intrusive igneous activity, transgressive bathyliths and stocks of massive granite, granodiorite and more basic rocks, with corresponding hypabyssal types, being injected through almost the whole extent of the folded area. The intrusions are girt with contact-zones of hornfelses, and commonly accompanied by a

FIGS. 1–12.—The Tasman Geosyncline at various periods. (The stippling indicates the probable areas of deposition, marine and terrestrial. Close stippling indicates the probable positions of geanticlines.)

1. Cambrian; 2. Ordovician (with Benambran geanticline); 3. Silurian (with Bowning geanticline); 4. Lower and Middle Devonian (with Tabberabberan geanticline); 5. Upper Devonian and Lower Carboniferous (with Kanimblan geanticline); 6. Upper Carboniferous; 7. Lower Marine Permian; 8. Upper Coal-measure Permian (with Hunter-Bowen geanticline); 9. Triassic; 10. Jurassic; 11. Cretaceous (Aptian); 12. Eocene.

characteristic suite of economic minerals including ores of tin, molybdenum, tungsten and bismuth. Where the igneous rocks are not visibly intrusive into Upper Devonian or Carboniferous beds their age can sometimes be inferred from the associated ore-minerals, but in certain parts of New South Wales and Victoria distinction from the petrologically similar intrusives of Tabberabberan age is difficult. No Upper Devonian or Lower Carboniferous beds are known in Tasmania, but massive granites, etc., with the suite of minerals characteristic of the Kanimblan ore-region are fairly widely distributed, and there can be little doubt that, as suggested above, the geosyncline extended south to include the island. Here the granites were preceded by considerable comagmatic intrusions of basic and ultrabasic rocks which brought in chromite and osmiridium. What appears to be the northern limit of this subsidiary Tasmanian ore-province is marked by the serpentine intrusions of Waratah Bay in the south-east of Victoria.

The Kanimblan diastrophism very drastically reduced the size of the geosyncline, and later Carboniferous deposition was confined to eastern Queensland and New South Wales (Fig. 6, p. 630). The rocks are both marine and terrestrial, the latter including great thicknesses of glacial and fluvioglacial as well as of volcanic material. Some of the tillites, however, are marine, and a few small fossiliferous marine lenses appear among the terrestrial beds. Evidently the sea lay partly on and partly just off the east coastal strip of Queensland and New South Wales and made short-lived incursions into the bordering swampy lowlands.

Permian Period

One of the most controverted questions in Australian geology is that of the position of the boundary between Carboniferous and Permian systems, but fortunately in the present connection this is not of vital concern, since no orogeny took place between the Kanimblan and Hunter-Bowen disturbances, though there is much evidence of vertical movement. Where a continuous section is exposed the Carboniferous beds, largely glacial and fluvioglacial, pass up into marine beds containing species identical with or similar to those found higher up in definitely Permian beds. Provisionally the base of the Permian (corresponding roughly, perhaps, to the base of the Sakmarian of Russia) may be drawn at the point of entry of the first marine fossils of Permian aspect.* That the

* Recognising that the lowest of these marine beds might be Upper Carboniferous despite their faunal content, the late Sir Edgeworth David suggested the system-name *Kamilaroi* for the whole of the reputed Permian sequence.

glaciation lingered on into Permian time as thus defined is proved by the presence of occasional glacial erratics in the marine beds. In Queensland no known exposures afford a clear and continuous section from Carboniferous into Permian beds, but a few sections suggest a conformable passage. According to the view here adopted the terrestrial glacial beds of Wynyard on the north coast of Tasmania, Bacchus Marsh and elsewhere in Victoria, and the southern parts of South Australia, are Upper Carboniferous possibly passing up into Permian, but apart from the first they were apparently not deposited within the Tasman geosyncline.

In Upper Carboniferous time Tasmantis may have been temporarily joined to Australia by swampy lowlands; these, however, were gradually submerged by the Lower Permian seas, which spread over them to north, west and south (Fig. 7, p. 630). The Permian sequence gives evidence of great rhythms of deposition, a lower and an upper marine shallow-water series alternating with freshwater coal-measures. The later sea spread beyond the confines of the earlier, and the lowland swamps wherein the upper coal-measures were laid down extended in their turn far beyond the limits of the seas, particularly in Queensland. Comparative faunal studies suggest that communication with the north was broken during Permian time. (Fig. 8, p. 630.)

In eastern Australia the Palæozoic Era was closed by the *Hunter-Bowen* orogeny, which began near the end of the second Permian marine epoch, probably a little after the end of the Artinskian, and was renewed at the very end of the period. The folding force had its greatest effect in the east where, in addition to the Permian, the Carboniferous and Devonian rocks which had escaped deformation during the Kanimblan orogeny were folded with an intensity which diminished from east to west. Compression was relieved by upthrusting or overthrusting along a great arc (Fig. 8, p. 630) concave to the west and stretching from Townsville (Queensland) to near Newcastle (N.S.W.). A second zone of upthrusting parallel to the first and some 40 miles east of it is seen along the western border of the New England Highlands in New South Wales, and in south-eastern Queensland there are signs, though not so clear, of a similar eastern thrust-zone. The relief afforded was such that the Permian beds lying west of the main thrust-zone were at most only gently folded. Quite a considerable proportion of the Permian strata of Queensland and New South Wales lies beyond the main thrust-zone, and those of Tasmania are entirely outside it.

The later phases of the Hunter-Bowen movement were accompanied by invasions of magma. Serpentines and gabbros appear

in the eastern thrust-zone, but the chief expression of igneous activity is seen in great composite bathyliths of granitic and allied rocks in north-eastern New South Wales, and in similar but much smaller intrusions in Queensland. Many of the component rock-types are very closely comparable to those of the Kanimblan bathyliths and are accompanied by a similar suite of ore-minerals, but their restriction to the belt of late Permian folding and their intrusive attitude towards Permian strata serve to distinguish them.

Mesozoic and Cainozoic Eras

With the initiation of the Hunter-Bowen orogeny marine deposition in that part of the geosyncline lying within Australia and Tasmania virtually ceased. During the coal-measure epochs Tasmantis and Australia may have been joined, but probably in Upper Coal-measure time the locus of marine deposition had moved permanently to the east over the Tasman Sea, and then in the Mesozoic Era only the western margin of the geosyncline, wherein sedimentation was almost entirely lacustrine, lay over the coastal lands of Queensland, New South Wales (Figs. 9, 10 and 11, p. 630), and Tasmania.* In Upper Triassic time there was a slight and transient marine transgression in the vicinity of Sydney, and during the Cretaceous Period the sea temporarily encroached in south-eastern Queensland, in Neocomian time near Rockhampton and again in the Aptian farther south in the vicinity of Maryborough. During this second invasion the Tasman geosyncline was in communication with the epeiric sea that stretched from the Gulf of Carpentaria to the Great Australian Bight.

Though the course of Mesozoic sedimentation was punctuated by occasional vertical crustal movements, there is no record of orogenesis till an indeterminate epoch within Upper Cretaceous time, when the *Maryborough* movement folded the Cretaceous and other Mesozoic strata in the coastal area of south-eastern Queensland with intensity diminishing westward, as well as the Jurassic, Triassic and some Permian strata in the coastal belt of New South Wales. In Queensland folding was accompanied by some overthrusting and followed by plutonic invasion on a relatively small scale.

The Maryburian orogeny marked the end of the Tasman geosyncline within the continent of Australia. Its subsequent history cannot be directly traced, but we may reasonably suppose that in

* No account is here taken of the Triassic and Jurassic lacustrine beds of Victoria or the Permian coal-measures of the Riverina district (N.S.W.), which, it is thought, were deposited in basins lying west of and quite independent of the Tasman geosyncline.

Tertiary time it was situated entirely in the area now occupied by the Tasman Sea (Fig. 12, p. 630), and indeed the known existence of a Main Divide in the eastern Australia of Tertiary time, approximately coinciding with that of the present day, with rivers flowing east as well as west, implies the existence of a sea marginal to and somewhat beyond the present faulted coastline. The final extinction of the geosyncline probably came about through the late Tertiary or Pleistocene fracturing and foundering which led to the break-up of Tasmantis, the isolation of New Guinea, New Caledonia, New Zealand, Fiji, etc., and the formation of the Tasman and Coral Seas.

Summary and Conclusion

From its extent, its duration in time and its eventful history the Tasman geosyncline must surely rank as one of the greatest of its kind that the world has ever seen. It lay wholly or in part upon the Australian continent throughout the Palæozoic and Mesozoic Eras, and experienced many tectonic vicissitudes as the result of which its boundaries, the locus of maximum deposition, and the facies of its deposits changed repeatedly. In earlier Palæozoic times its size and situation were probably more or less constant, but the great Kanimblan diastrophism drove the sea permanently far to the east, and through this and the two subsequent foldings Australia may be said to have been built up and extended eastward to a little beyond its present coastal limits. Bryan and Jones have stressed the point that in post-Devonian times all the sedimentation was bathyalic, and it may be noted that after the Tabberabberan orogeny terrestrial deposition became increasingly important. It is quite impossible to say how much sediment was laid down within the geosyncline, but a rough calculation based on the maximum known thickness of rocks belonging to each system yields the stupendous total of more than 22 miles.

Among the deposits volcanic rocks play an important rôle, but at present it is not possible to relate the different types closely to tectonic and other conditions. Spilitic and keratophyric rocks, for example, are associated with certain Cambrian, Silurian and Devonian radiolarian cherts, marine limestones, etc., but the same or very similar types are found amid littoral marine and even lacustrine sediments of Permian and Carboniferous age, and on the other hand are notably absent from among the Ordovician graptolitic shales. Andesites, toscanites and rhyolites are prominent among the terrestrial Devonian and Carboniferous deposits but appear also among Silurian marine sediments.

Of particular interest is a small group of trachyandesitic and

trachybasaltic rocks contemporaneous in the shallow-water Upper Marine and Upper Coal-measure Permian beds of New South Wales, with cognate monzonitic intrusives, from some of which through contamination and magmatic differentiation rare and extreme alkaline types have arisen.

Mesozoic sedimentation was notably devoid of volcanic incident apart from occasional showers of ash, except in the rather unstable area of south-eastern Queensland, where rhyolitic and andesitic lavas and pyroclastic material were poured out at intervals.

The orogenic epochs were for the most part marked by bathylithic injection and ore-deposition within the geanticlinal belts. Certain areas, particularly that comprising north-eastern Victoria and the country across the border in New South Wales, suffered magmatic invasion during three and possibly four of the Palæozoic disturbances.

A certain correspondence may be observed between the recorded diastrophisms and those of extra-Australian regions. The Upper Cambrian folding may be a counterpart of the Killarnean of North America if, as some have contended, the latter is of Cambrian and not of pre-Cambrian age. The Benambran orogeny may be compared with the Taconic of North America and the Bowning with the Caledonian (*sensu stricto*) of Great Britain and Europe, while the Tabberabbera disturbance may have synchronised with that responsible for the unconformity between Upper and Lower Old Red Sandstone. The Kanimblan orogeny appears to have been contemporaneous with the Sudetic of Europe and the Hunter-Bowen with the Saalian and Pfalzian and with the Gondwana disturbance of South Africa and South America. Both Kanimblan and Hunter-Bowen fall within the interval embraced by the Variscan movements. The Maryborough folding, possibly coinciding with the culmination of the American Laramide orogeny, and the Cainozoic foundering of Tasmantis, belong to Stille's Alpine Period of diastrophism.

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ELECTRON MICROSCOPY

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In the last fifteen years the electron microscope has grown from the earliest model, with a resolving power about equal to that of the best optical microscope, to its present form in which its performance is not far short of that which is regarded on theoretical grounds as its ultimate limit [1]. With existing commercial microscopes it is possible to obtain a practical resolving limit of about 30 ångstroms, a figure some fifty times smaller than for a good optical microscope.

It is natural to expect that the use of such an instrument will add much to our knowledge of the fine structure of material objects, and it is proposed in this article to give some account of the kinds of information which can be and have been given by the electron microscope, and of the nature of techniques which have been devised to provide objects suitable for the instrument.

Electron microscopes may take as many general forms as do their optical analogues. There are, in particular, transmission, reflection and dark field instruments, in which the screen illumination is due to the portions of the electron beam which are respectively transmitted, reflected or scattered. Of these forms, the transmission electron microscope is potentially the most versatile and it alone has been sufficiently developed to be regarded as a definite instrument.

Many descriptions [2] have been published in recent years of the details of the mechanical arrangement and of the electron-optical design of typical electron microscopes, and it is not proposed to say anything here on the subject further than that the transmission electron microscope in its present form consists essentially of (1) a source of constant velocity, high-voltage electrons which illuminate the object, (2) an " objective " (usually but not always a magnetic lens) which produces an enlarged " electron image " of the object, (3) one or more " projector " lenses which serve to produce a further enlarged image on (4) either the fluorescent viewing screen or a photographic plate.

Provision is usually made to control the direction, convergence and intensity of the illumination and to control the alignment and power of the lenses. A suitable portion of the image can be selected and focused on the fluorescent screen, and a permanent record is

almost invariably made by exposure to the beam of the photographic plate, which is placed in a position equivalent to that of the screen.

It is usual to record the image at magnifications of between 2000 and 20,000; quite the largest proportion of micrographs are taken at magnifications between 5000 and 10,000. At a higher magnification, the intensity on the screen can be made sufficiently great for easy viewing and convenient recording only at a risk of subjecting the object to a perilously high beam intensity. The grain of modern photographic plates can be fine enough to allow detail as small as 30 Å to be portrayed at a magnification of 10,000. Such a plate is conveniently inspected directly by means of a viewing box and a high-power magnifying glass.

The electron-microscope image of a real object presents the same general appearance as does an optical micrograph. The detailed appearance varies according to the composition and structure of the specimen. The contrast in the final image comes from the varying capacity of different parts of the object for preventing the incident electrons from forming a correctly focused image at the screen. Local darkening of the focused image may arise as the result of electrons which are lost from the beam because they are scattered outside the effective periphery of the lens, or as the result of electrons which, on account of loss of energy in the specimen, or excessive inclination to the lens axis, are diffused over a wide area of the image. The complete absorption of high-voltage electrons in the commoner types of electron-microscope specimen is rare, and this mechanism contributes inappreciably to the contrast. The effective periphery of the lens is sometimes set by the presence of a real stop, but more often because the lens field fails to deflect electrons incident with more than a certain finite obliquity into the image field.

When small objects, such as particles of fine powders, are suitably supported in the field of view, they usually pass little of the beam unmodified and appear as black silhouettes against a bright background. Finer particles, such as smokes, give similar general patterns, but show some transparency to the beam, especially where the particles occur naturally as thin platelets.

A screen picture of sorts can be obtained from a very large variety of objects, provided that the specimen contains at least some areas in which the solid matter is so dispersed as to allow the incident beam to pass relatively unhindered. It by no means follows, however, that all such objects show detail comparable in size with the resolving limit, and two special conditions must be

satisfied before detail on this fine scale can be delineated: the specimen must contain details differentiated by changes of electron scattering power, since otherwise there is no inherent source of contrast, and the specimen must not contain scattering matter in such quantity that the final image is confused by a welter of electrons which have so far lost their original direction or velocity as to fall, after deflection by the lens, irregularly into the image field.

Small particles of gold a few tens of ångstroms thick, supported on a very thin film of collodion, form a specimen that meets the special conditions and lead to an image of high resolution. These conditions are not normally fulfilled, for example, by a supported micro-organism, which may well be both too thick and too uniform in electron scattering power to give an image of adequate contrast.

In the application of the electron microscope to a specific field of research the essential problem is, of course, to devise a technique of selecting, preparing and mounting the specimen so as to give the maximum of information in the screened picture. Before describing such techniques in detail it is appropriate to draw attention to a number of special limitations and difficulties of electron microscope technique. Firstly, the electron microscope is essentially a vacuum device, since the electron beam is not able to pass freely through air. Specimens must have a vapour pressure low enough to remain stable in a vacuum of 10^{-4} mm. of mercury. Specimens which in their normal state contain water, such as most, if not all, micro-organisms, are necessarily desiccated on insertion into the instrument. The process of desiccation leads to some distortion and possibly to serious damage to the specimen. This hazard raises special difficulties in the biological fields.

Objects used in the microscope undergo continual bombardment and may therefore be subjected to considerable heating. Where the specimen is a bad conductor of electricity there is, in addition, risk of mechanical damage arising from the forces which accompany the accumulation of charge on the surface. It is essential to guard against these risks by minimising both the intensity of the beam and, at the same time, the exposure of the object to the beam.

A notable advantage possessed by the electron microscope lies in its great depth of focus. The high resolution forms of the optical microscope use objectives of large numerical aperture (*ca.* 1·4) and have a depth of focus comparable in magnitude to the resolving limit; in consequence a field of only 0·1 μ is in focus at any one time. Very many objects have a considerably greater depth than this; for example, a bacillus is seldom much less than 1 μ. With such objects only a part is in focus at any one time, and the screen image

is inevitably overlaid with diffuse light from out-of-focus adjacent planes. Electron microscope objectives have extremely low numerical apertures (*ca.* 0·002) and the depth of focus is a few microns. The large depth of focus can be turned to good account in the taking of stereographic photographs of thick objects, from which the arrangement in depth of the structure can be found in a simple and reliable way. More will be said on this subject at a later stage.

The transmission type of electron microscope can be used with either bright-field or dark-field illumination. In practice, however, very few examples of dark-field illumination are to be found in the literature. The chief difficulty lies in the provision of an appropriate stop. There are two possible arrangements: one involves the use of a central stop at the back-focus of the objective just large enough to trap the beam, the other illuminating the object with a slightly oblique beam, the main beam being trapped by the aperture-stop of the object-lens (i.e. the "objective aperture"). In the former case, the stop must be not more than 1 or 2 microns wide and is therefore difficult to construct. The illustrations shown in Plate I, Figs. (*e*) and (*f*), show cotton fibres supported on a copper grid, photographed respectively with light and dark field illumination. Both are photographed with an objective aperture, the illumination in the latter case being inclined to the axis at an angle of about ½°. The relatively poor resolution in the case of the dark-field photograph is mostly due to a preponderance of incoherently scattered electrons in the radiation which falls in the open aperture of the lens.

Specimens

In almost every case specimens suitable for investigation by electron microscopy are mounted in the microscope on small grids or perforated discs which are designed to give maximum support. The individual apertures through which the illumination falls are 50 to 100 microns wide, and these unobscured areas are alone imaged on the screen. The specimen itself may take any of a variety of forms; the principal of these are described as follows: objects supported by grid, objects supported by a thin film, very thin sections, and thin film replicas.

Objects supported by Grid.—Fibrous objects can frequently be supported directly by the grid so as to allow transmission micrographs to be made of the objects. Where the object is thick, the image has the appearance of a silhouette, but thinner portions of the object are usually transparent and show internal detail. Speci-

mens such as fine threads, Wollaston wires, quartz fibres, sharp ends of tungsten wires, portions of sharp edges of blades and profiles of fine crystal grains, can each be investigated in this manner.

Certain smokes, particularly those formed so that the particles aggregate into long chains, can be prepared so as partially to overhang the grid bars from which they are supported. Oxide smokes of zinc, magnesium and molybdenum are readily prepared in this form, and the corresponding micrographs are remarkable for the clear evidence which they furnish of the very regular crystalline nature of these smokes.

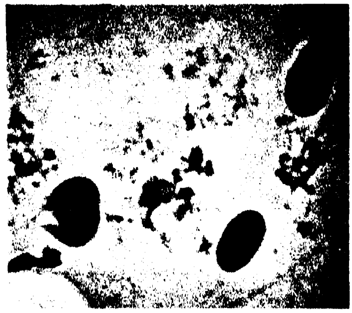
The siliceous skeletons of diatoms and the fine regular structures which form the wings of insects can in many cases be supported directly on the grid. Fig. (*a*) shows an electron micrograph of a portion of a fly's wing, supported directly on a fine-mesh (200 to the inch) copper grid. Small hair-like structures are seen to be attached to a more or less continuous film.

Objects supported on a Thin Film.—The commonest method of mounting specimens is to support the small objects which are to be investigated on a very thin film, which in turn is mounted on a grid. Suitable films may be prepared in many ways, but in every case the film must have as little scattering power as is consistent with the necessary strength.

The material most often used for the purpose of film-making is collodion. Films of about 100 ångstroms thick are formed by allowing a drop of 2 to 3 per cent. solution of nitro-cellulose in amyl acetate to spread over the surface of water in a bowl. Such films are reasonably strong. They are ordinarily free from visible structure and can be prepared and handled with ease and consistency. A film 100 ångstroms thick scatters a 50 kV. electron beam just sufficiently for a difference in tone between the two sides of a film edge to be perceptible on an appropriately exposed photographic plate. Such a film is strong enough to support large particles without undue risk of breaking. Cast films of " Formvar " (polyvinyl formal) have also been used to a considerable extent. They are considered to be mechanically stronger and to have much less water absorption than collodion films prepared by spreading on water. Most commercial plastics can be formed in films thin enough to be usable as supporting films, but little systematic investigation appears to have been made of their relative suitabilities. Silica films, prepared by evaporating fused silica on to a flat plastic substrate and dissolving away the substrate, are also used as supporting films.

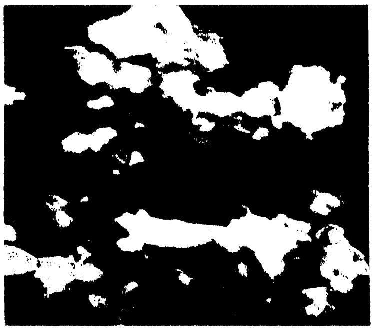
Many fine powders, such as pigments for the paint industry,

(a)

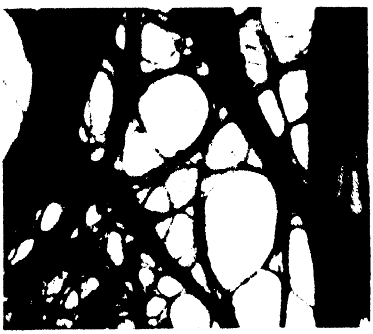


(b)

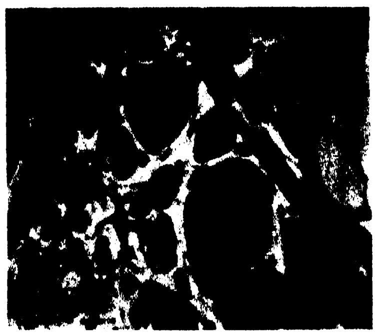
(c)



(d)



(e)



(f)

(*a*) Object supported on grid: portion of fly's wing, magnificatio (*Courtesy of Metropolitan-Vickers Electrical Co.*)

(*b*) Object supported by film: spores of *B. Subtilis*, magnification 8000 ×. (*Courtesy of National Institute for Medical Research.*)

(*c*) Surface replica in Formvar: nickel chromium steel, etched to show Intermediate Transformation Product, magnification 700 ×. (*Courtesy of National Physical Laboratory, Crown copyright reserved.*)

(*d*) Shadow-cast: clay particles mounted on film and shadow cast at an angle $\cot^{-1} 6$ with gold, magnification 10,000 ×. (*Courtesy of English Clays Lovering Pochin & Co.*)

(*e*) and (*f*) Bright-field and dark-field electron micrographs of same field: cotton fibres supported on grid, magnification 5000 ×. (*Courtesy of Metropolitan-Vickers Electrical Co.*)

dyestuffs for the textile industry, and rouge for the plate glass industry, contain particles too small in size to be resolvable in the ordinary optical microscope. The industrial effectiveness of such powders may depend markedly on the distribution in size and shape of the smaller particles. Such material can be investigated in the electron microscope, and for this work it is usual to prepare a sample of material on a supporting film, since the continuous smooth surface of the film can be covered by an appropriate process more or less uniformly with a sample of dispersed particles.

Micro-organisms form a large and important class of objects and can in many cases be supported with advantage on a film. Virus bodies and the smaller bacteria can be prepared by drying off from an aqueous suspension. The size of such bodies is sufficiently small for many to be contained in a single field of view of the instrument, and many examples of micrographs of this type of object are to be found in the literature. See Fig. (*b*).

Specimens in the Form of Films.—Where a specimen itself forms a very thin film, as in the case of rubber, of plastics in general, and of biological membranes, the specimen can usually be supported directly by the grid. Similar transparent films, which can also be used directly as objects, can sometimes be made by forming a film from a dispersion of the small particles of a specimen in a film-forming medium such as collodion or rubber solution. Films of this sort are ordinarily prepared on a glass plate and stripped mechanically from the surface. The method forms a convenient way of producing a stable dispersed selection of fine particles for investigation of particle size distribution. It suffers, however, from the disadvantage that the particles are imbedded during observation in a scattering medium which completely surrounds the particle and therefore reduces the image contrast to some extent. This latter effect is more important in the case, for example, of particles of an organic compound of low scattering power than in the case of dense mineral particles.

Sections.—Section techniques, such as are used in biological work, are at least in principle applicable to the electron microscope. Films of a typical imbedding medium, such as collodion, which have a thickness much greater than 0·1 microns, have much too great a stopping power to allow effective imaging by means of 50-kV. electrons, and a section of such material should therefore not be much thicker than 0·1 microns.

With a conventional microtome it is difficult to cut sections as thin as 1 micron and the production of sections of one-tenth of this thickness requires special technique. Methods have been devised, notably by von Ardenne, whereby a standard microtome has been

adjusted by arranging to tilt the stage progressively during the cut so as to produce thin wedge-shaped specimens. In this fashion the thinnest edge of the wedge is occasionally thin enough to be used as an electron-microscope specimen. Similarly shaped specimens can be obtained by cutting obliquely through the interface of a composite block formed by the embedded specimen and an overlying layer of material such as gelatine and then dissolving away the gelatine in hot water to leave a wedge of specimen.

A much more satisfactory approach to the problem of producing suitable sections lies in the design of new and more effective microtomes. A number of special microtomes have been built in the last few years for this purpose and have met with at least some success. In each case the cutter, which is usually rotating, has been arranged to travel at much higher speed than in conventional instruments. At this increased speed the inertia of the specimen and of the knife system makes the cutting system effectively very rigid. It is probable that the success of high-speed microtomes is due at least as much to a higher precision in the relative motion of the knife and specimen during the cut as to the extremely high cutting speed. This precision microtome work is still at an early stage and further progress may well be expected in the next few years. Such work as has been completed has usually involved thick sections ($0 \cdot 5\ \mu$) and in order to obtain reasonable contrast in the image it has been necessary to use the otherwise rather inconvenient aperture-stop.

Surface Replicas.—In view of the very low penetrating power of 50-kV. electrons, the transmission electron microscope cannot be used to form images of very thick objects. Information relating to the shape of the surface of such objects can be obtained by use of an accurate replica of the surface structure made in the form of a film thin enough itself to form the object for the electron microscope. The local thickness of the replica film, and therefore the density of the corresponding part of the electron micrograph, varies in simple relation with the shape of the surface. The micrograph therefore gives a pictorial impression in changes of height of the surface.

There are two desirable characteristics of the replica: (*a*) ability to take a faithful impression of the original surface on one of its faces, but to retain a flat second face, (*b*) possession of such chemical composition as to have an optimum scattering power. Films of very low or very high scattering power material would show little contrast; the former would tend to be uniformly transparent and the latter to be opaque.

The simplest form of replica is that obtained by casting a solid

film from solution on to the specimen surface and stripping off the film. One of the most successful of such processes is the Formvar [3] method. Formvar is a hard plastic which dissolves in a suitable solvent (dioxane) to form a weak solution which can be spread as a thin layer over the specimen surface. For very smooth surfaces, such as clean glass, the solid film formed after evaporation of the solvent can be teased off under water. Where the film holds more tenaciously, as in the case of etched surfaces, the film can often be removed by stripping from the surface a short length of thin, adhesive tape which has been made to adhere to the film. More drastic methods of freeing the film are the forcing off of the film by contraction of a drying gelatine coating to the film and, in the case of extremity, the dissolving away of the specimen. See Fig. (*c*).

The silver-collodion and the polystyrene-silica [4] methods are successful, but more elaborate, forms of replica technique. The first method consists in forming a thick film of silver by evaporation *in vacuo* on to the specimen. The film is stripped mechanically from the object and the surface of the silver then coated with a thin film of collodion. The silver is finally dissolved away in nitric acid so as to free the collodion replica. This replica technique was one of the earliest to be developed, but now appears to be little used. The polystyrene-silica method has been used with considerable success, particularly on etched surfaces, in metallurgy. The prepared specimen is mounted in a block of polystyrene, for example, by heating under pressure in a standard metallurgical mounting press. The mould is separated from the specimen and the surface of the mould coated by evacuation *in vacuo* with a film of silica a few hundred ångstroms thick. The silica film which forms the replica is freed from the polystyrene by solution of the latter in an appropriate solvent. The micrographs which result from polystyrene-silica replicas show great clarity of detail. There is, however, some difficulty on occasion in interpreting the finer detail of the silica replica photographs, as the rear surface of the replica, far from taking the ideal flat form, has—as might be expected from the nature of the evaporation process—much the same surface shape as the original specimen. Variants of the polystyrene-silica method have been used successfully to provide replicas of soft materials.

Specimen Technique.

A considerable amount of useful information can be obtained by direct-transmission electron micrography of simply supported specimens. The graduations of tone in the final picture are almost

invariably great enough to give a good general impression of the shape and structure of the object. By the elaboration of special techniques, much more information relating to the shape and disposition of the various parts can be obtained. Some of the more important techniques are described below.

Stereoscopy.—Where the object possesses sufficient contrast to give a sharply detailed image the simple transmission picture gives little indication of the structure in depth. In view of the large depth of focus of the image, it is possible to take pairs of photographs of any particular field with slightly different inclinations of the specimen plane to the lens axis. Such stereoscopic-pairs can be viewed in a stereoscope, and it is possible to determine the structure of the object in three dimensions from the appearance of the image. Numerical measurements can be made of the elevations of parts of the specimen by determination of parallax or by the use of an appropriate stereometer. The stereomicrographs are obtained by tilting the specimen between successive exposures, preferably without removal of the specimen from the microscope.

Shadow-Casting.—A special technique, generally known as shadow-casting, has been devised for use with the electron microscope and has added considerably to the usefulness of the microscope, especially in the investigation of surfaces. The method consists in evaporating on to the specimen *in vacuo*, from an oblique angle, a collimated beam of atoms of a heavy metal (*i.e.* a material with a very high scattering power). The beam falls on the object itself and increases the opacity of the object. The supporting film, which lies obliquely to the beam, receives a thin layer of metal over most of its area, but remains completely clear in the geometric shadow behind all elevated portions of the surface. A specimen prepared in this fashion gives an electron-microscope image in which the structure in depth is shown in relief; the visual impression is closely similar to that which would be obtained on looking at a similar specimen illuminated by parallel light falling in the same direction as the gold beam. The pictorial effect is most striking and the general interpretation of the shape of the structure is immediately clear (Fig. (*d*)). Apart from the obvious evidence that the shadow-cast conveys of relative height in the surface, the method has the great advantage that the surface shape is mapped out by means of variations in thickness of a film of very high scattering power, and in consequence the screen image possesses very high contrast. Much surface detail shown by this method is quite invisible in the corresponding ordinary transmission photograph. The shadow-casting method has been used with great success in the

biological field, particularly by Wyckoff [5], who has prepared specimens showing the detailed structure whereby virus bodies are packed into a crystal lattice.

Shadow-casting gives information relating entirely to surfaces of objects and adds nothing to knowledge of the internal structure of the object; this property can be used with advantage in order to remove ambiguities which otherwise may exist in the interpretation of surface replicas. The process is particularly suited to replica work since it also increases the contrast.

Miscellaneous Techniques.—One of the main difficulties which faces the experimenter in the preparation of objects consisting of fine powders is the production of proper dispersion of the particles.

Finely dispersed powder specimens can be produced either by blowing the powder direct into a cloud, which falls on the specimen, or by spraying a liquid dispersion through an "atomiser." Specimens of dust or of smoke may be precipitated directly on to a film by gravitation, or by electrical or thermal precipitation. These methods in general may be no more than qualitative, and a considerable amount of investigational work is required before any detailed deductions can be made about the relative frequency of occurrence of particles in given size ranges.

The commonest approach to the formation of samples of fine material is to disperse the material in water and to dry off the water from a drop of the suspension which has been deposited on a thin supporting film.

The initial stage of forming a fine dispersion may be facilitated in some cases by subjecting the suspension to violent mechanical agitation or to an intense supersonic field. In the case of powders which do not form stable aqueous suspensions, good stable dispersion can sometimes be obtained by the use of a "wetting agent." In the course of the drying process the smaller particles tend to clump into large aggregates, and the major part of the clumping is due to a scavenging effect of the liquid meniscus as it finally contracts on the surface of the supporting film. Some success in overcoming the difficulty has followed the coating of the supporting film before use with a monolayer of, for example, egg albumin. It is considered that in this way it is possible to obtain a large force of adhesion between the particles and the contracting meniscus.

Two other distinct approaches offer some attraction. The first is to disperse the sample in a solution of, for example, collodion and thereby to retain the liquid dispersion during the drying-out process. This has already been referred to. The second method is to make a stable aqueous suspension, to freeze the suspension and

to remove the water from the solid specimen by means of vacuum sublimation (freeze-drying). During this drying process the particles are never mobile and no opportunity is presented for them to form into clusters.

Numerous special techniques have been devised in order to cope with specified subjects. For details of these, reference can readily be made to the rapidly growing technical literature [6]. Many of these, such for example as the enclosure of the organism between the two collodion films, the "electron-staining" of the organism with osmic acid or photo-tungstic acid (the latter process has been used successfully in the study of the structure of muscle), refer to the specially difficult task of preparing effective biological objects for the microscope. Suggestions have been mooted for overcoming the severe treatment which may accompany the desiccating effect of the vacuum on a small organism by enclosing it in a "closed cell." Such a "cell" must provide a normal environment for the organism and must be capable either of withstanding a large pressure difference across its walls, as in the case of an aerobic specimen, or alternatively of preventing any substantial diffusion of water through its walls, as in the case of an anaerobic specimen. As far as the author is aware, no successful cell of this variety has been constructed and used with effect, and something of the difficulty of the project becomes apparent when one appreciates that in the case of an anaerobic specimen the depth of water of 1 micron necessary to envelop even a small organism is too great to allow effective penetration of a 50-kV. electron beam.

By careful technique, such as the "controlled drying" method devised by Smiles of the National Institute for Medical Research, the uncertainty in interpretation due to distortion on drying of biological specimens can be minimised. There seems little doubt that the usefulness of the electron microscope in the biological field in particular will depend very much on the provision of special techniques.

Interpretation of Results

There is close agreement of general appearance between a low-magnification electron micrograph and a high-magnification optical micrograph in the case of thin objects. Such comparisons have been made with diatoms, fibres, powders, and replicas of etched metal surfaces. The coarse detail, consisting of outlined areas of greater or lesser opacity to the beam, is usually as readily interpreted as the corresponding detail in an optical micrograph.

Interpretation of the small detail is more open to dispute, and

in this field the surest practical guides to correctness are consistency of features in successive micrographs and experience of the relevance of conclusions drawn from the interpretation.

Apart from artefacts produced by the mode of preparation of the specimen, the two main difficulties which arise are the interpretation of detail shown inside the boundary of a partially transmitting specimen and the determination of the nature of the particle boundary. In specimens with no regular crystalline structure in their components, and such specimens are all too rare, a definite relationship is to be expected between the local brightness of the plate (or blackness of the print) and the mass density of the object. For a homogeneous object this means that the blacker patches of the print represent the thicker parts of the object. Such a simple relation does not hold in general for crystalline specimens, since the regular structure can lead to a high concentration of intensity in a diffraction beam which leaves the object at an angle much greater than is on the average involved in the case of simple scattering. Crystalline objects may present the appearance of opaque or of transparent objects according as the diffracted beam falls outside or inside the effective aperture of the objective; slight changes in orientation between closely situated similar particles may lead to one appearing as a dark and the other as a light object. These diffraction effects make it very difficult to determine from the photograph whether the particle is irregular in thickness or merely distorted in its lattice structure. Difficulties of this sort can be reduced by using either stereoscopy or shadow-casting technique in addition to that of simple transmission, and these three techniques in combination will usually allow unique determination of the structure at least of the external shape of the object. It is, however, very difficult to distinguish between the possibilities of a discrete internal structure and of a regular, but slightly distorted, crystalline structure with which is associated diffraction anomalies; some evidence relating to the reality of apparent detail comes from observing whether the image appearance remains unaltered as the direction of the illuminating beam is changed by a small amount.

When observation is made of detail on a scale approaching that of the resolving limit of the objective, the precise nature of the image formation, as instanced by the shape of the image of a sharp edge, depends upon the type of aberration effective in limiting the performance of the objective. Where the diffraction effects predominate over the geometric aberrations the position of the corresponding geometric boundary may well be flanked with diffraction bands. These bands may form the counterpart of the higher order

maxima of the Airy diffraction pattern, as in the case of a correctly focused image, or they may be Fresnel fringes as in the case of an out-of-focus image. Where the geometric aberrations, in particular the spherical aberration, are large the fine structure typical of the diffraction system tends to be obscured. In such cases the boundary may still be skirted with a bright contour which derives from the distribution of intensity in the slightly defocused image formed of components of the illumination which have suffered either excessive deviation or slight loss of velocity in passing through the specimen. The general characteristics of the contour effects are readily recognised by an experienced micrographer, but failure to appreciate the possibility of their existence has sometimes led in the past to the assignment of one or more fictitious exterior coatings to an otherwise simple object.

There are a number of special difficulties in interpretation which arise through peculiarities possessed by the microscope itself. The energy intensity at the specimen may well be so high as to cause changes to occur in the specimen. With most available microscopes it is possible to obtain such a beam intensity as to melt the wires of the supporting grid, and it is therefore clear that there is considerable risk of melting and possibly volatilising parts of the specimen. If photographs are obtained as soon as practicable after the insertion of the specimen, it is usually possible to reduce this effect to negligibly small proportions, particularly if the beam intensity is kept as low as possible and exposures of the order of a minute are used. There is also good reason to suspect that in certain cases the specimen may become contaminated by decomposition products of oil vapour from the diffusion pump. Such contamination can be prevented by inserting a cold-trap between the pump and the main instrument.

The problems of interpretation and the inevitable defects of existing techniques do not seriously limit the usefulness of the electron microscope, and these problems are in any case such as one has to solve in connection with the use of most modern physical instruments.

The author wishes to express his thanks to the following people for the provision of photographs: Mr. J. Smiles and the Director of the National Institute for Medical Research for Plate I (*b*), Mr. F. W. Cuckow and the Director of the National Physical Laboratory for Plate I (*c*), and to Mr. A. J. Morcom of the Research Laboratories and the Directors of English Clays Lovering Pochin & Co. for Plate I (*d*). The author also wishes to thank Mr. B. G. Churcher, Manager of the Research Department, and Sir Arthur P. M. Fleming,

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SCIENTIFIC METHOD AND EDDINGTON'S FUNDAMENTAL THEORY

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Sir Arthur Eddington was one of the principal participants in the debate on the rôles of " deductive " and " inductive " methods in physical science which has been in progress during recent years. Since he had always maintained in this controversy that his views were demanded by the results of scientific investigation, it is pertinent to enquire what light his posthumous *Fundamental Theory* [1] sheds on the subject.

Principally it presents Eddington's ideas on the theory of physics as a coherent and comprehensive scheme. In conjunction with *The Philosophy of Physical Science* [2] and an article " The Evaluation of the Cosmical Number " [3] the new book makes clear the " epistemological " basis of Eddington's physics. This latter paper was to have formed the basis of an unwritten chapter on " Epistemological Theory " in *Fundamental Theory*. It is a matter of great regret that Eddington was unable to write this chapter, as it seems likely that he would have settled several awkward questions.

The orthodox view concerning the nature of scientific knowledge is that the hypotheses at the base of a scientific theory are entirely dependent on experiment for verification. Eddington's view was that fundamental physical theory is deducible from premisses which are methodological in character. Eddington calls his major premisses " epistemological principles " ; we may describe them as " statements about physical method."

A fundamental principle of " scientific epistemology " is that every item of physical knowledge is an assertion of what has been or would be the result of carrying out a *specified* observational procedure. Eddington has called this principle an axiom, but it is more than that—it is a rule by which every honest physicist abides. To get his set of epistemological principles Eddington unearths the rules by which the physicists play their game. Among these are the methods of interpretation used by physicists, which, according to Eddington, are :

1. Observational knowledge is formulated as a description of a universe. We call this the physical universe.

2. A very general method is that of analysis, by which the physical universe is represented as consisting of a number of parts.

3. All variety is regarded as a challenge to further analysis; so that the ultimate end-products of analysis can only be identical units, the variety originating in the way the units are put together. This is the atomic concept.

4. The analysis requires that some parts and characteristics have a degree of permanence.

5. Elementary physical systems are considered to be isolable, but yet observable.

We are now in a position to develop Eddington's theory—in doing so we shall be implicitly assuming the five concepts outlined above. Measurements are the tools of physics. A measurement involves four entities, two to furnish the observable that is said to be measured and two to furnish the comparison observable used as a standard. When we measure a distance the extension between two given objects is compared with the extension between two marks on the standard scale. What we measure is something associated with four entities. This is called a "measurable."

The most primitive entity we can contemplate has neither parts nor magnitude. It has no parts, for it is primitive and unanalysable. It has no magnitude, for magnitude is an attribute of a measurable. An "entity" is to be thought of in this theory in roughly the same way as a point in Euclid's geometry. The only property of a primitive entity is that of existence or non-existence in the structure contemplated. Eddington associates with a primitive entity a symbol whose meaning only becomes definite when it is conjoined with another symbol representing the structure contemplated. Only two definite meanings are possible. Technically a definite meaning is called an eigenvalue. The two eigenvalues of an entity are a yes-eigenvalue and a no-eigenvalue.

The most primitive measurable is provided by four primitive entities whose existence attributes are independent. It will not exist unless all four entities exist. Since each entity has two eigenvalues, a measurable has $2 \times 2 \times 2 \times 2 = 16$ eigenvalues, of which only one is a yes-eigenvalue. Four entities provide us with a variety of things to measure. This array of measures is called a tensor measure. Several measurables may have the same tensor measure; thus several sticks may have the same length and weight.

Although measurables with the same measure have the same quantitative properties, they are conceived as qualitatively distinct. This qualitative distinction is introduced in accordance with the

concept that variety originates in the structure and not in the elements; the distinction between different measurables can be made structurally by means of a mathematical device called a "rotation group." We therefore pick from the known rotation groups the one in which the rotations are symbols with 16 eigenvalues. This is the group which defines the "EF frame" on which Eddington's physics is based. The E's and F's are hypercomplex sets of 16 square roots of -1. The tensor measures are also now taken to be EF-numbers. From this EF frame or "sedenion algebra" with its measurables and tensor measures the whole scheme of theoretical physics can, it is claimed, be deduced. Crudely speaking, then, a measurable has 16 eigenvalues, the necessity for 16 eigenvalues leads to the EF frame, and from this fundamental physics can be constructed.

Having seen the path, we will try to clear up some of the obscurities in the argument. What Eddington is doing is building a structure—part of the structure of the physical universe. Abstract structure can be described by the methods of symbolic algebra; these methods define a structural pattern by the inter-relations of a closed group of symbolic operations. It is a very important property of these structural patterns that, when the groups have been completed, each part is defined in terms of the others and the whole so built up that the different parts can be distinguished from one another. To illustrate this: we said earlier that four entities provide us with a variety of things to measure, and that this array of measures was called a tensor measure. This implied that there were different properties to measure, and that the different measures could be distinguished. The structure is built from measurables with their tensor measures, and then defines what these measures are and how they are distinguished.

Let us examine the physics Eddington deduces from the sedenion algebra. The method is to develop the mathematical properties of different elements of the structure, and then to identify these elements with the subject matter of physicists' observations. The first stage is to show that the E-numbers, whose components represent physical characteristics, can be represented by vectors in a "4-space," one of whose dimensions differs from the other three. This "space" is identified as ordinary physical space-time. This basic identification limits the number of ways in which other components may be identified. In making these identifications Eddington is guided by the results of ordinary physical theory; thus one component is identified as mass or energy, in accordance with the usual view of the interconvertibility of mass and energy.

This identification of the elements of the analysis with ordinary physical quantities is an essential link between the theory and observation, which we shall consider further when we deal with the implications of the theory for scientific method. The whole scheme of theoretical physics now follows from the sedenion algebra, without the introduction of any empirical results. This is not to suggest that Eddington could have developed his theory without the results of relativity and quantum theory, but rather that the hypotheses of current relativity and quantum theory are contained in the sedenion algebra.

Eddington's deductions, however, transcend relativity and quantum theory; they solve mysteries which current theory was unable to tackle. The theory deduces both the forms and numerical constants of the laws of gravitational and electrical fields. More than this, it explains the nature of gravitational and Coulomb forces—they are different aspects of the indistinguishability of the elementary particles, which is a direct consequence of the third of the methods of interpretation mentioned above. The theory explains why electric charge exists only in definite units, and why it is always associated with definite masses such as those of the proton and electron.

A fundamental result is the calculation of the "cosmical number," "the number of particles in an Einstein world which is composed of hydrogen and which satisfies the requirements of quantum theory" [4]. This result ($\frac{3}{2} \times 136 \times 2^{256}$) is of more than casual interest, as it determines the ratio of electrical to gravitational forces between particles, the range and magnitude of non-Coulombian forces, and cosmical repulsion. Applications of the basic theory give nuclear mass defects, the magnetic moments of hydrogen and the neutron, and the mass and life time of the cosmic ray meson. The range of results covered by the theory is remarkable and the agreement with experiment is excellent.

What has Eddington done? Apparently he has deduced the laws of physics from a consideration of the methods of interpretation and of measurement; in fact, the whole theory might well be called a theory of measurement. Eddington himself summarised his procedure in this way: "All our results are derived from the condition that the conceptual interpretation which we place on the results of measurement must be consistent with our conceptual interpretation of the process of measurement." [3] It is opportune to say now that Eddington did not claim to deduce the whole structure of the physical universe from the rules of measurement. Physical knowledge contains, besides the laws of Nature, a vast amount of special

information about particular objects surrounding us. The size of the earth, the weight of a motor-car, the mains voltage are all special facts, and certainly are not deducible in this way.

In discussing the theory and its relation to the scientific method, we will take no account of any possible logical errors inside the theory. What we have to discuss is the status of the methods of interpretation and the procedure of identification. The two are intertwined as the above quotation from Eddington shows. The point at issue was raised by Susan Stebbing in *Philosophy and the Physicists*, when she attacked Eddington for saying that "granting the identification is correct, the laws (of conservation) are mathematical identities. Violation of them is unthinkable." Miss Stebbing says there is nothing logical is making this identification—in making the identification you are assuming the answer. This criticism would certainly be valid if the laws were based on hypotheses; but the problem is more subtle for laws based on methodological premisses.

To see the difficulty, let us grant for the moment that the methods of interpretation are necessary for any theory of physics and are not just a set of hypotheses chosen to give empirical agreement. The fundamental particles are indistinguishable, and consequently in studying a group of them we shall get confused as to which is which. Eddington examines this interchange effect and computes its dynamical consequences. The effect of the indistinguishability is identical with that found empirically for Coulomb forces. Eddington therefore identifies interchange energy * with Coulomb energy. The quandary is now clear. If you have indistinguishable particles there will be certain observational effects.

Again, consider the third of the methods of interpretation. It is incontrovertible that in physics we analyse, and that we regard all variety as a challenge to further analysis. But what sort of finality are we prepared to accept? Is it necessarily one in which the relata are all the same, and the differences occur in the way the relata are put together? The whole status of the methods of interpretation seems one for considerable study, whose outcome I shall not presume to decide. However, there would seem to be three possibilities. The methods of interpretation may be either based on empirical success, or unique and necessary for any physics, or arbitrary methods used by all physicists.

If the methods are empirically based, then Eddington's physics is a scheme developed from hypotheses, and has the same status as any other theory of physics, albeit a unifying theory of great

* This is not quantum mechanical exchange energy.

importance. Its certainty is not better than inductive, and Miss Stebbing's identification criticism is justified.

If the methods of interpretation are presuppositions of the way we make our ordinary physical identifications, they are not physical hypotheses in the ordinary sense, and they may be either unique and necessary or arbitrary. The significance of the latter possibility is that it implies that theoretical physics is simply a matter of convention. In either case the laws of physics are a necessary consequence, and would appear to have a certainty better than that attainable by inductive methods. Eddington expressed his own view when he wrote : " We have to show, not that there are N particles in the universe, but that any one who accepts certain elementary principles of measurement must, if he is consistent, think that there are " [3].

If we accept Eddington's view there are some interesting consequences to notice. For instance, ordinary physical theory describes phenomena, whereas in an important sense fundamental theory explains them. Again, if there are undiscovered parts of physics, these parts should be hidden in the sedenion algebra. The rôle of observation is strictly necessary only for us to understand the meanings of the terms employed, and to make sure that there have been no logical errors in the arguments. Despite this, the experimental physicists will no doubt continue to produce results which the scientific epistemologist had not anticipated !

We may express our surprise that it is possible by any scheme of speculative building to erect the structure of physics on so few foundation stones : but in view of the undeniable achievements of Eddington's theory we are bound to take it seriously. We may leave it to the philosophers to decide whether, even if the laws of physics are necessary, we are driven to accept Eddington's near-Kantian philosophy.

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RECENT ADVANCES IN SCIENCE

ASTRONOMY. By A. Hunter, Ph.D., F.R.A.S., Royal Observatory, Greenwich.

Stellar Magnetism.—Though the existence of a general magnetic field on the sun had long been suspected, both by analogy with the earth and because of the characteristic structure of the solar corona noticed during total eclipses, it was not until 1913 that Hale obtained at Mt. Wilson Observatory the first indication of the Zeeman effect in certain Fraunhofer lines from the undisturbed disk. Further work at Mt. Wilson seemed first to confirm the earlier results, though the smallness of the Zeeman displacements measured (of the order of one-hundredth the widths of the lines) was always a weak point of the work. Certain subsidiary conclusions, however, notably that the field strength decreases rapidly with increasing height in the solar atmosphere, were regarded with suspicion at the time and have been criticised since.

It was particularly unfortunate that when the work was repeated during the years of minimum solar activity in 1922 and 1932, inconsistent results were obtained. At this stage a certain uneasiness about the conclusions was hard to resist—a doubt not, perhaps, about the existence of the field but about the quantitative assessment of its strength. Hale himself always wished to get further confirmation of his work with more powerful apparatus and improved methods of measurement, but he died with the project uncompleted.

If any such doubts still lingered, they should now have been removed by the publication (*Annales d'Astrophysique*, **9**, 101, 1946) of a remarkable piece of work by Thiessen on the subject. Abandoning Hale's method of measuring directly the very small Zeeman shifts in spectrum lines (largely, one gathers, because of the uncertainties of estimating small displacements on photographic plates), Thiessen uses a visual null method in which the displacement is compensated artificially. Light from the particular part of the sun to be examined is first passed through a quarter-wave plate. This changes the circularly polarised Zeeman components of each Fraunhofer line into components polarised in two planes at right angles. The light is then passed through a half-wave plate and a polaroid film before it is allowed to reach the slit of a concave-grating spectrograph used as a monochromator. The half-wave plate is rotated four times a second by means of a synchronous motor, so that the two components illuminate the slit in turn.

A second slit in the focal plane of the spectrograph isolates the immediate neighbourhood of the line to be examined, and the monochromatic light then passes to a Fabry-Perot interferometer, which produces a system of dark rings on a bright background. These interference fringes are observed visually to undergo in general a radial pulsation, of period one-quarter that of rotation of the half-wave plate, indicating that minute changes of wavelength are occurring in the light reaching the first slit. When this light originates at the sun's equator or at the poles, where the lines of force are perpendicular to the line of sight, no pulsation occurs; elsewhere on the central meridian some oscillation can be detected, reaching a maximum at heliographic latitude 45°. The extent of the pulsation will clearly depend on the wavelength separation of the Zeeman components and hence on the magnetic field, but, instead of attempting to measure it, the observer counteracts it by adjusting the amplitude of a synchronous oscillation (of opposite phase) in the air pressure between the interferometer plates. This pressure variation (of a few tenths of a millimetre of mercury) is produced by a pump, the amplitude of whose piston is variable and can be read on a scale. This scale is graduated directly in gauss by means of a subsidiary calibration using a laboratory source placed in an artificial magnetic field of adjustable intensity.

By stopping the rotation of the half-wave plate and diminishing the pressure oscillation, the sensitivity of the apparatus can be estimated: the lower limit of the measurable field strength for the iron line 6173 Å. amounts to about 10 gauss. Preliminary measurements of this line and a green chromium line agree in giving the strength of the sun's field at the pole as 53 ± 12 gauss, a figure coinciding almost exactly with Hale's value for low-level lines. The new measurements do not, however, confirm the rapid decrease in the field with height in the solar atmosphere. A much more extensive investigation is promised, using a variety of lines of different intensity at various points on the solar disk, and thus exploring fully the dependence of the magnetic field on height above the surface and on heliographic latitude. It is already possible to say of the method, however, that it is a piece of first-class observing technique of a kind that would have delighted Hale's heart.

It is incidentally just as well, perhaps, to have this confirmation of the magnitude of the sun's magnetic field. Theorists have recently tended more and more to invoke the field in examining the trajectories of particles in interplanetary space, whether they are interstellar particles falling in towards the sun or corpuscles ejected from the sun and travelling out towards the earth. It is

particularly fortunate that Thiessen's work, whilst confirming Hale's numerical results for the surface field, does away with the bogy of rapid radial limitation of the field, for some recent papers have assumed that at planetary distances the field is equal to that of an equivalent dipole at the sun's centre. Alfvén's theory of the origin of the planets, for example (*Stockholms Observatoriums Annaler*, **14**, No. 2, 1942; **14**, No. 5, 1943; **14**, No. 9, 1946), depends entirely on the rather complicated paths followed in this field by interstellar particles in the outer parts of the solar system. A still more recent theory due to Hoyle (*The Observatory*, **67**, 123, 1947) attributes the excitation of auroræ to electrons which are ejected from solar chromospheric flares and which, after travelling from the sun at the relatively low speed of ejection (this is given by the long delay of about a day between the flare and the associated aurora), pick up the necessary penetration energy in a region where the magnetic field of the sun, regarded as a dipole field, is comparable to that of the earth. Astrophysicists on the look-out for some way of treating the intractable problems presented by clouds of charged particles moving in interplanetary space will thus welcome Thiessen's results as clearing up what was a rather doubtful matter. Though his measurements refer specifically only to the field at and near the sun's surface, the extrapolated values at planetary distances obtained by assuming the sun to be a uniformly magnetised sphere seem to be confirmed by the spiral motion of ionised matter in comet tails (*Popular Astronomy*, **54**, 268, 1946).

Meanwhile, however, the question of magnetism in celestial bodies has gone beyond the confines of the solar system. It is a tenet firmly held by astronomers that the sun is a pretty average sample of the stars as a whole; that (broadly speaking) any type of star in the sky could be matched by the sun if due allowance is made for differences of distance, mass and surface temperature. The suggestion that stars might have magnetic fields is therefore no revolutionary idea once it is accepted that the sun has one. It is one thing, however, to postulate the existence of stellar fields; it is quite another to detect and measure them. As far back as 1915, though, Hale was hoping that the then new 100-in. telescope might be able to detect such fields. The first detailed suggestions for a programme of observation were not made till 1937, when Minnaert pointed out (*The Observatory*, **60**, 292, 1937) that the magnetic effects which in the sun appear as differences between individual points of the disk are not necessarily blotted out in all stars by that integration over the entire visible hemisphere which is inevitably imposed by distance.

Minnaert suggested that, as in Hale's experiments, a circular analyser should be placed in front of the spectrograph slit and rotated by 90° steps so as to extinguish alternately light circularly polarised in each sense. Lines affected by magnetic broadening would then have their red and violet Zeeman components suppressed in turn, and differential measurements of consecutive spectra would afford a means of measuring the field strength. On the assumption that the magnetic and rotational axes of a star will coincide, Minnaert points out that if the line of sight is perpendicular to this common direction, no polarisation will be observable, for the two halves of the disk will produce equal and opposite effects that annul one another. But for an observer looking *along* the axes, integration over the hemisphere now visible will give a net effect that does not vanish. In this case, calculation shows that the differential shift for a dipole field reaches one-third of the optimum displacement expected for a hypothetical observer who could resolve the stellar disk and who could accordingly choose the most favourable individual point of that disk to examine. Minnaert gave it as his opinion that if stellar fields ten to twenty times as strong as the solar field exist, they should be detectable on modern high-dispersion spectrograms by this technique.

This remarkable prediction has now been verified. H. W. Babcock announces (*Astrophysical Journal*, **105**, 105, 1947 ; *Publ. Astr. Soc. Pacific*, **59**, 112, 1947) that magnetic fields of the order of 1000 gauss have been detected in the stars 78 Virginis, γ Equulei, β Coronæ Borealis, HD 125248 and a few others. In looking for suitable stars which might be expected to show a Zeeman effect, Babcock followed the suggestion, made as far back as 1891 by Schuster, that perhaps the magnitude of the magnetic field of a celestial body depends on its speed of rotation. Now it is well established from Struve's pioneer work in the 1930's that rapid rotation is a property almost exclusively of early-type stars. Equatorial peripheral speeds of the order of 100 km./sec. are observed for O, B, A and early F stars. Between F2 and F5 the observed frequency of such rotations rapidly decreases, and later types show none. (The sun at G5 is an exception merely because it is near to us. The rotational speed of a star is measured by the Doppler broadening produced in its spectrum lines. Since different parts of the stellar surface are moving relative to the observer at different speeds, they will give rise to lines differently displaced from the normal position. When the integrated light from all parts of the star is examined, these displaced components are observationally superposed to give a composite undisplaced line whose breadth

measures the speed of rotation. The sun, of course, shows a visible disk, and light can be isolated from the limbs; its equatorial speed of 2 km./sec. is much lower than can be detected by the cruder method enforced for stellar work.)

In any search for rotating stars, however, an awkward complication arises because rotation is not the only cause of line broadening in stellar spectra. Some early-type stars, for instance, show the very fine lines now believed to be due to the low surface gravities characteristic of supergiants; conversely the abnormally broad lines in white dwarfs may be due to pressure (*i.e.* Stark) effects produced by the intense gravitational fields in these bodies. If, however, attention is confined to the hot main-sequence stars, it is still true that in addition to the majority that show rotationally broadened lines there are a few that show narrow lines. This is just what would be expected for a stellar population in which the axes of rotation are distributed at random; there will be a few stars observed "end-on" for which the rotation, even if it is present to the same extent as in the average early-type star, merely produces velocities across the line of sight and thus no Doppler broadening. The search for observable magnetic fields can thus be narrowed to stars of early type in the main sequence showing narrow metallic lines (hydrogen or helium lines are sensitive to Stark effect). A further indication would be the presence of incipient emission, which, as Struve has shown, may indicate an "extended shell" atmosphere produced by rapid rotation.

If in such a star the magnetic axis coincides with the rotational axis and the field over the hemisphere presented to the observer is distributed as it would be over a uniformly magnetised sphere, it can easily be seen qualitatively that the Zeeman effect should be present in lines absorbed in the star's atmosphere. For although the surface field at the equator is opposed to that at the pole, it is of only half the polar magnitude, and the field vector is perpendicular to the axis not at 45° but at 36°; thus the component of the field parallel to the axis, when integrated over the visible hemisphere, differs from zero. Furthermore, limb darkening tends to suppress the equatorial contributions to the integrated Zeeman pattern and thus to enhance the net effect.

It will be recalled that in the normal inverse Zeeman effect, a line observed along the field is split into two components equally displaced, in opposite directions from the normal position of the line, by an amount proportional to the field strength, these components being circularly polarised in opposite senses. As the field vector becomes inclined to the line of sight, an undisplaced plane-

polarised component appears and the displaced components are elliptically polarised. As observed through an analyser for circular polarisation, then, the centre of gravity of an unresolved line will shift as the inclination between the field and the line of sight alters. The light coming from the star will of course not be characterised by a unique value of this inclination, but when integration is carried out over the whole visible hemisphere, full account being taken of the projected areas of the various latitude zones, of the limb darkening, and of the variation in strength as well as in direction of the field with latitude, it remains true that the centre of gravity of the blended pattern will shift on changing from a right-handed to a left-handed circular analyser. Babcock has carried through the integration and arrives at the conclusion that if δ is the displacement of the centre of gravity in frequency units,

$$\delta = \pm\, 0{\cdot}31aH$$

where H is the polar field strength and a the displacement of the normal satellite for unit field, and the sign is determined by the sense of the analyser. Thus the integrated effect is about one-third as great as it would be if light from the pole alone could be isolated. Transforming to wavelength shifts $\Delta\lambda$ and inserting the Lorentz value $a = 4{\cdot}67 \times 10^{-5}$ cm.$^{-1}$ we get

$$\Delta\lambda = 1{\cdot}45 \times 10^{-5}\lambda^2 H$$

This corresponds to a shift of 0·003 Å. in the blue region of the spectrum for a polar field of about 1000 gauss. For the so-called anomalous Zeeman effect the shift is larger by a factor depending on the atomic transitions involved in the production of the line, this factor reaching as much as 2 or 3 for some lines.

Babcock's observations were made with a circular analyser in front of the slit of the high-dispersion (2·9 Å./mm.) coudé spectrograph of the 100-in. telescope. The analyser produces simultaneously two spectra, oppositely polarised, side by side on the plate, so that differential measurements effectively double the displacements to be measured. If lines of Zeeman factor 1·5 are used, a shift of least detectable amount, say 0·0015 mm. for repeated measurements, would be produced by a field of 500 gauss. This is the observational limit until measurements can be extended to the red or infra-red (note that $\Delta\lambda \propto \lambda^2$).

The first good plates of 78 Virginis showed for some lines relative displacements which were visible with a hand magnifier, amounting to as much as 0·010 mm. between the right-handed and left-handed spectra. It is always difficult to be sure, however, in delicate

measurements of this sort that the displacements are real, so a series of checks was applied. It was found

(a) that reversal of the analyser reverses the sign of the displacements;
(b) that the displacements in Å. are independent of the dispersion used and of the type of analyser employed;
(c) that no displacements occur when light from a terrestrial arc source is admitted to the spectrograph instead of light from a star; and
(d) that no displacements occur in the spectrum of ε Pegasi, a K0 star for which no rotation is observed and thus no magnetic field nor Zeeman effect is expected to exist.

These conclusions, taken together, indicate both that the displacements found are indeed due to the Zeeman effect and that their numerical values are not systematically affected by spurious effects introduced by the apparatus.

Babcock exhibits his results by plotting measured displacement against theoretical Zeeman effect for over 100 lines in 78 Virginis between 3800 Å. and 4800 Å. In view of the delicacy of the measurements the correlation shown is impressive; and it must be considered fully established that the polarisation found in the absorption lines of this star can be fairly interpreted as due to the Zeeman effect. For a Zeeman factor of 1·00 (*i.e.* for lines showing the normal effect) a differential displacement of 0·009 Å. is found at 4600 Å. This corresponds to a polar field of 1500 gauss, some three times the observational limit.

This investigation was carried through on the basis of a number of simplifying assumptions, three of which in particular must be carefully scrutinised before the results can be accepted at their face value. First and second, that the magnetic axis is in the line of sight, and that it coincides with the rotational axis. These are based on a somewhat attenuated line of reasoning which associates rotation with magnetisation in the star. The almost universal prevalence of rotational broadening in early-type dwarf spectra makes it fairly certain that 78 Virginis is no exception to the general rule, particularly as the proportion of sharp-line stars is numerically no more than would be expected if the rotational axes are distributed at random in space. Doubtless, then, the star is observed "end-on" as far as rotation is concerned. The assumed coincidence of the two axes is more doubtful—there is a divergence of 6° in the sun and 12° in the earth—but evidence referred to below associating the two effects suggests that it is not an unreasonable first approximation.

The third assumption is that the star is spherical; a condition that is manifestly incompatible with rapid rotation. As Babcock points out (*Publ. Astr. Soc. Pacific*, **59**, 114, 1947), oblateness will produce two effects. Firstly, since the surface brightness at any point is proportional to surface gravity, the pole of an oblate spheroid will be brighter than the equatorial regions, a factor which will conduce to over-estimating the field since it will over-weight regions where the field is strongest. Secondly, the integration will be affected, since the dependence of the field on latitude will not be that of a uniformly magnetised sphere. It seems impossible to assess the importance of this effect, since the rotation is not observable but is inferred statistically; but it can hardly alter the order of magnitude of the results unless the rotation is to become so fast as to make the star dynamically unstable.

We must conclude, then, that the observed displacements are due to a magnetic field of the order deduced; but is it established that this field is indeed a general magnetic field and not one due (say) to the stellar analogues of sunspots on a vaster scale? For an answer to this question we can appeal to the sun. Though the fields of sunspots are much more intense than the sun's general field, even at solar maximum spots involve only a few thousandths of the area of the photosphere at any time (and are, area for area, less bright too), and they are correspondingly ineffective in producing the Zeeman effect in integrated light. Moreover, they tend to occur in pairs exhibiting opposite polarity. Unless the conditions on stars are very different from those on the solar surface, then, it is hardly conceivable that large spots could do more than produce a broadening of the stellar lines distinguishable from rotational broadening only by its different dependence on wavelength. The possibility that a residual polarity of the magnitude found could be the result of stellar spots may be dismissed if further observations show that the observed field does not vary with epoch.

It is difficult, then, to resist the conclusion that those metallic-line A-type stars suitable for showing the Zeeman effect do in fact possess general magnetic fields of the order of a thousand gauss at their surfaces; and, by an inevitable generalisation, that other similar stars showing broad lines possess similar fields, though they cannot be observed because of an accident of geometry. This raises once again, and more insistently, the old question of whether magnetism and rotation are not indissolubly connected with one another. It has long been known, for example, that the ratio of the magnetic moment P to the angular momentum U of the earth is closely the same as that for the sun. Babcock (*Publ. Astr. Soc.*

Pacific, **59**, 112, 1947) and Blackett (*Nature*, **159**, 658, 1947) have now examined whether the same constant of proportionality holds for 78 Virginis.

The question is complicated because no accurate values for the radius, mass or angular velocity of the star exist, and the best that can be done is to assume mean values from statistical evidence for other similar stars. The two authors adopt rather different values, and their results give an indication of how accurately the proportionality holds :

	P gauss-cm.^{3}	U gm. sec.$^{-1}$ cm.^{2}	P/U
Earth	$8 \cdot 0 \times 10^{25}$	$7 \cdot 1 \times 10^{40}$	$-1 \cdot 11 \times 10^{-15}$
Sun	$8 \cdot 9 \times 10^{33}$	$1 \cdot 12 \times 10^{49}$	$-0 \cdot 79 \times 10^{-15}$
78 Virginis (Babcock) . .	4×10^{36}	$4 \cdot 1 \times 10^{51}$	$\pm 1 \cdot 0 \times 10^{-15}$
78 Virginis (Blackett) . .	$2 \cdot 1 \times 10^{36}$	$2 \cdot 6 \times 10^{51}$	$\pm 0 \cdot 81 \times 10^{-15}$

(The signs in the last column indicate that though the directions of rotation of the earth and the sun are similarly related to their magnetic moments, the sense of the ratio is unknown in 78 Virginis since the direction of spin is unknown.)

Clearly the quantities P and U are proportional over a measured range of nearly $10^{11} : 1$. Noting that P/U is equal in order of magnitude to the quantity $\sqrt{G}/c$, where G is the gravitational constant and c the velocity of light, Blackett suggests that the equation

$$P = \beta G^{\frac{1}{2}} c^{-1} U,$$

where β is a small numerical constant of order 0·3, must be taken seriously as a possible new general law of Nature for all massive rotating bodies. It does indeed seem unlikely, in view of the large range of the variables involved, that the approximate fulfilment of the equation is accidental. Its simplicity, Blackett remarks, contrasts strikingly with the arbitrary complexity of the theories hitherto put forward to relate the magnetic fields of the earth and the sun ; and the occurrence of only the macroscopic constants G and c in the constant coefficient seems to exclude, except by way of a remarkable numerical accident, the possibility that the magnetic fields of these bodies are determined by the specific properties of the matter composing them.

Nevertheless, the validity of the linear relation depends on three points only, and one would like to see the intervening gaps filled in satisfactorily. There seems little to be gained in the direction of increasing angular velocities, for if the rotational speed inferred for 78 Virginis is increased by a factor of more than four,

dynamical instability will be reached. The best chance here would probably be to observe some of the emission-line B stars investigated recently by Struve and his collaborators. There is reason to believe that the emission arises in circumstellar rings shed in the course of rapid rotation. Unfortunately the observations are likely to be troublesome to interpret if emission and absorption lines are present, for the direct and the inverse Zeeman effects will have to be disentangled.

Both Blackett and Thackeray (*The Observatory*, **67**, 105, 1947) have pointed out the importance of observations of a partial eclipse in a binary star showing rotational broadening in its spectrum. If it should prove possible to measure both the Zeeman effect and the Doppler shift in the light from the nearly eclipsed edge of the rear component of an eclipsing binary, the magnitude and direction of both the magnetic field and the rotation could be measured directly, instead of having to rely on statistical rotations, which can at best give the order of magnitude of the rotation and never its sense.

It was noted above that the measured range in P and U reached nearly $10^{11} : 1$. The corresponding range in field strengths, however, is only about 2000 : 1. Blackett has pointed out that if, as seems possible, white dwarfs are formed by the collapse of main-sequence stars to very dense cores, their angular momenta, and thus on his hypothesis their magnetic moments, will be of the same order as those for main-sequence stars. Sirius B, for example, has the same mass as the sun but only 0·02 of its radius. Its surface magnetic field ($H = 2P/R^3$) will thus be 50^3 times greater, and will therefore reach 6×10^6 gauss at the pole. Surface fields of a few million gauss will produce Zeeman broadenings of a few dozen ångstrom units, so that the observed widths of the Balmer lines in white dwarfs, which are of this order, may be due in part to large magnetic fields as well as to the big Stark effects hitherto invoked to explain them. Polarisation measurements in white dwarf spectra will decide whether there is any substance in this train of argument, and if so, how much of the width is due to Zeeman broadening. There will then be another point to log on the plot of magnetic moment against angular momentum, and further evidence on which to decide whether Blackett is indeed right in claiming that this relation may provide the long-sought connection between electromagnetic and gravitational phenomena.

PHYSICS. By F. A. Vick, O.B.E., Ph.D., F.Inst.P., The University, Manchester.

Barrier-Layer Rectifiers.—The phenomenon of asymmetric conduction across certain metal-nonmetal boundaries has been studied for a long time, perhaps even before Schuster's experiments of 1874 (*Phil. Mag.*, Vols. 47 and 48). The development of the reliable "metal rectifier" now in large-scale use has, however, taken place during the last twenty years only, and the theories most generally accepted are less than ten years old. Even now, theory has yet to account for many of the properties of barrier-layer rectifiers.

The most important types of metal rectifiers are (*a*) copper-cuprous oxide, (*b*) metal (*e.g.* a low melting-point alloy)—selenium, (*c*) magnesium—resistance layer—cupric sulphide, (*d*) crystal—"cat's whisker." The first three are made in disk or plate form, and the current is carried across a large area. In type (*d*), the current passes through a fine point of the metal wire resting on the crystal, in a manner familiar to early wireless enthusiasts. It is of interest to observe in passing that this type, in an improved form, *e.g.* with a germanium crystal and tungsten wire, found important application during the late war in the rectification of very high frequency currents.

The manufacture of large-area cuprous oxide and selenium rectifiers has been described by A. L. William and L. E. Thompson (*J.I.E.E.*, Pt. I, **88**, 353, 1941). Here practice has preceded theory and most of the processes have evolved from trial-and-error methods. For the cuprous oxide rectifiers, pure copper disks about 1 mm. thick are heated in air to just over 1000° C., with one side protected, for about 10 minutes to form a cuprous oxide film on the other side. The oxide film is then about 0·1 mm. thick. The disk is annealed, and any black cupric oxide formed on top of the red Cu_2O is removed by mechanical or chemical means. An electrical contact is made to the surface of the Cu_2O by a coating of colloidal graphite and then a soft metal, or by spraying the surface with a suitable metal. The effective rectifying junction is the Cu-Cu_2O one. The efficiency of the rectifier is sensitive to impurities.

The support for the selenium rectifier is normally a roughened steel plate, sometimes superficially nickel-plated. Selenium is applied by one of the standard methods and converted by heat treatment to the β variety, which is crystalline and has a lower electrical resistance than the α or γ forms. The counter-electrode metal is then sprayed on top, to form the rectifying junction. The

metal used is a low melting-point alloy, and its composition affects the properties of the rectifier. A small percentage of thallium is said to have a great influence. The selenium in its pure form has a very high resistance, so small quantities of other substances are added, such as halogen compounds. The completed rectifier is "formed" by passing a current of about 50 mA. per sq. cm. in the reverse direction (see below) for a few minutes.

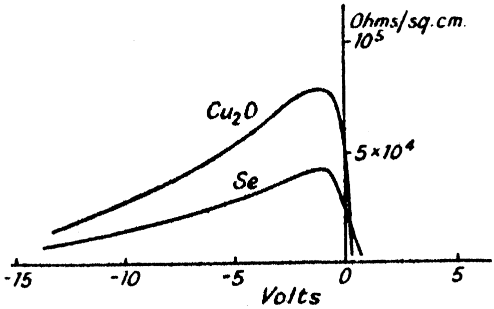

FIG.

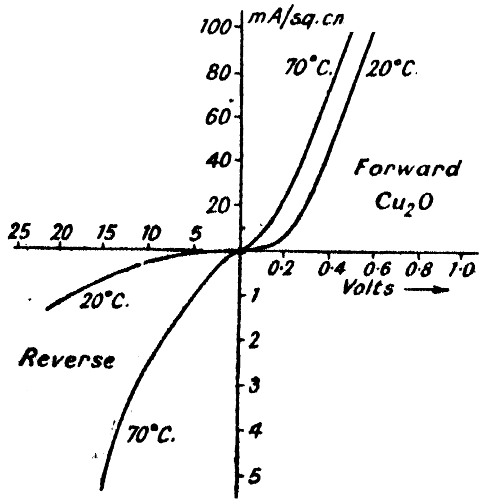

FIG. 2.

The general forms of the voltage-resistance and voltage-current characteristics of large-area rectifiers are well known, and are indicated in Figs. 1 and 2. Note that the scales of Fig. 2 are different in the "forward" and "reverse" directions. In Fig. 1 the "resistance" is defined as V/I, *i.e.* the ratio of the instantaneous voltages and currents. Ohm's Law is not obeyed at low applied voltages. In general, the resistance depends on time as well as tempera-

ture, and the characteristics are subject to reversible "creep" and irreversible "ageing." When considering detailed behaviour the exact conditions of measurement and the previous history of the rectifier must be specified. Creep and ageing are complex phenomena and will not be considered in detail here. The current in both directions increases with increase in temperature.

All the metal rectifiers mentioned involve semi-conductors, and before considering theories of rectification it is necessary to review the electronic properties of semi-conductors. These are distinguished from metallic conductors by three main criteria: (*a*) a lower, but still appreciable electrical conductivity, (*b*) conductivity increasing with increasing temperature, instead of decreasing, (*c*) conductivity often increasing with increasing concentration of certain impurities, instead of decreasing. These properties are best interpreted in the light of a potential energy diagram, Fig. 3. The top line in (*a*) and (*b*) represents the potential of an electron at rest in free space away from the solids, and is taken as zero, and in both diagrams the shaded band represents the range of energies of electrons bound to the atoms or ions in the lattice (the "full band") and F a forbidden region of energies. C is the "conduction band" giving the allowed energies with which an electron may migrate through the solid and be influenced by an externally applied P.D. to give a current. This band is of width χ, normally less than one electron volt. To reach the conduction band from the filled band the bound electrons would have to acquire an energy of one or more electron volts, which would demand an extremely high applied electrostatic field (10^7–10^8 volts per cm.) or a high temperature. In semi-conductors there are, however, a number of discrete additional levels within the normally forbidden region, and associated with "impurities" in the lattice, or lattice defects. A perfect crystal of a compound such as Cu_2O consists of regular arrays of positive and negative ions. Sometimes, however, the lattice may contain small numbers of impurity atoms in interstitial positions in the lattice, or there may be an excess or deficiency of one of the constituent atoms. In both cases, extra levels may result. There are two important cases:

(*a*) Electropositive atoms from the crystal lattice or foreign to the lattice trapped in interstitial positions. The valency electron of such an atom may be considered to be loosely attached to its positive ion and to have a potential energy within the normally forbidden band. Less energy is thus required to raise (thermally or otherwise) its energy to that corresponding to the conduction band, and it is such electrons which give rise to electrical conduction

in the semi-conductor. The extra "donor" levels are shown at L, in Fig. 3 (*a*), and solids in which they operate are known as "excess" semi-conductors, or, particularly in U.S.A., an "*n*-type" semi-conductor. If E electron volts is the energy corresponding to the step from L, to the conduction band, and N_0 the concentration of impurity centres, the number of electrons reaching the conduction band per second at absolute temperature T is

$$aN_0e^{-E/kT} \qquad (1)$$

assuming the Maxwell-Boltzmann statistics to apply. Then the electrical conductivity is found to be approximately proportional to

$$be^{-\frac{1}{2}E/kT} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(see Mott and Gurney, *Electronic Processes in Ionic Crystals*, 1940, Chap. V).

(*b*) The second important case is that in which a positive ion is missing from the lattice, and an electron is missing from one of

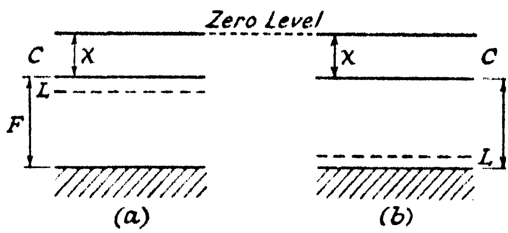

FIG. 3.

the associated negative ions. If this electron is replaced, it has an energy corresponding to a level L in Fig. 3 (*b*). The vacant place is a "defect electron," or more picturesquely "a positive hole." Thus in Fig. 3 (*b*) the levels L are normally empty, but may be filled by electrons from the full band, leaving a positive hole in a different place in the lattice. A positive hole can thus be said to migrate through the lattice, and the effect is as if a positive electron, with slightly higher mass than the normal electron but otherwise with the properties of an electron, carries the current in the solid when a field is applied. A semi-conductor of this kind is a "deficit semi-conductor," or a "*p*-type semi-conductor." The temperature dependence of conductivity is given by an expression similar to equation (2).

Excess and deficit semi-conductors may be distinguished by the sign of the Hall Effect. Cu_2O is a deficit semi-conductor when there is a deficit of Cu, and impure silicon an excess. The properties

of semi-conductors as such might well form the subject of a subsequent article in this series.

Many theories have been put forward to account for the properties of metal rectifiers, and some have been discarded as being untenable in the light of more recent experimental or theoretical work. One discarded theory has, however, been revived to some extent by A. Fairweather (*J.I.E.E.*, **89**, Pt. I, 499, 1942), who reconsiders what might happen when the contact between metal and semi-conductor is achieved at a number of points of comparatively small area only, the remainder of the surfaces being separated by thin gaps. If a small voltage (greater than the contact P.D.) is applied, the current will flow through the points of contact, and the relation between voltage and current will be linear. Since the total contact area is small, the P.D. across the interface will be larger than that across the semi-conductor or metal. If the applied voltage is increased, the P.D. across the interface will increase until the field in the gap becomes high enough for field emission from the negative surfaces of the gaps to become appreciable. Field emission (cold emission) from a surface depends on the applied field acting at the surface according to a relation of the form

$$i_F = BF^2 e^{-\frac{\phi^{3/2}b}{F}} \quad . \quad . \quad . \quad . \quad (3)$$

where F is the potential gradient and ϕ the work-function of the surface. As the voltage across the interface is increased, therefore, the current will increase rapidly. Eventually, at a very high voltage, the current is limited by the bulk resistivity of the semi-conductor, and in the limit the current is again proportional to the applied voltage. If the P.D. is reversed, the two proportional (linear) parts of the characteristic would be repeated, but the part governed by field emission would be different because of the difference in work function. (In any case the field emission from a semi-conductor does not necessarily follow the Fowler-Nordheim relation, equation (3).) On this view, the action of a rectifier depends on having the contact with one face of the semi-conductor of the form just described, and the other contact substantially without gaps.

Some characteristic curves of the type predicted have been observed, and the gap theory is able to account for some of the other properties of metal rectifiers, but by no means all of them.

We must now consider the modification to our energy-level diagrams when a semi-conductor is placed in contact with a metal. For simplicity, an excess semi-conductor will be used for illustration, though the same principles apply, with suitable modifications,

for deficit semi-conductors. Further detail will be found in the book by Mott and Gurney (*loc. cit.*). Fig. 4 (*a*) represents the relevant energy levels in metal and semi-conductor before they are placed in contact. ϕ is the work-function of the metal, and χ depth of the conduction band of the semi-conductor. χ is normally smaller than ϕ. If now the two are brought into contact, electrons which have high enough thermal energies, given by equation (1) for the semi-conductor and an analogous one based on Fermi-Driac statistics for the metal, will be able to surmount the potential barrier, now height $\phi-\chi$ electron volts. Since ϕ is greater than χ, more electrons will pass into the metal than from it, and equilibrium will be reached with the metal having a negative charge and the conduction band of the semi-conductor depressed as shown in Fig. 4 (*b*). Mott and Gurney have shown (*loc. cit.*) that the number of electrons crossing the barrier is the same in both directions when

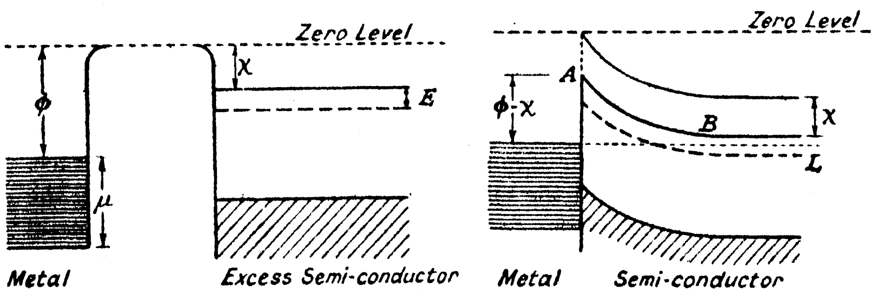

FIG. 4 (*a*). FIG. 4 (*b*).

the bottom of the conduction band in the semi-conductor is E/2 electron volts above the Fermi level in the metal.

If now an electric field is applied in such a direction as to depress the conduction band in the semi-conductor still further, the slope of the barrier, AB, is increased and its width decreased. On A. H. Wilson's theory (*Proc. Roy. Soc.*, **A136**, 487, 1932) of rectification the barrier becomes so thin that electrons may penetrate through it (the "wave-mechanical tunnel effect"). This gives the "forward" direction as the flow of electrons from metal to semi-conductor, which is, unfortunately, the wrong way round. The theory, at first sight so attractive, has other defects and has to be abandoned, though the possibility of the tunnel effect taking part in the flow of current must sometimes be borne in mind.

Mott (*Proc. Roy. Soc.*, **A171**, 27, 1939) starts from Fig. 4 (*b*) but postulates the existence of an insulating layer (*e.g.* pure Cu_2O without defects in the case of the cuprous-oxide rectifier) between

metal and semi-conductor, thin enough for conduction to be possible through it (see Mott and Gurney, *loc. cit.*, p. 168) but thick enough to prevent the wave-mechanical tunnel effect. If now a field is applied in such a direction as to raise the level of the conduction band in the semi-conductor, electrons will be able to flow more easily to the metal, but not from the metal. A field in the opposite direction increases the height of the barrier from the semi-conductor, but does not make much difference to the flow from the metal. In general principle, this gives an acceptable explanation of the rectifying action, though it leaves many points of detail to be explained. It is indeed possible to construct a barrier-layer rectifier with an artificial insulation layer, *e.g.* a thin coat of varnish on the metal, and it has been proved experimentally that most of the voltage drop occurs in the interface region. For a defect semi-conductor the explanation is very similar, but the current in the forward direction is carried by positive holes, and the direction of rectification is opposite to that with an excess semi-conductor, as is found in practice.

Schottky independently, but at about the same time as Mott, put forward a very similar theory of barrier-layer rectification, but without postulating an actual resistance layer at the metal surface. He examines in detail the effect of the positive space-charge in the semi-conductor resulting from the flow of electrons to the metal (see Fig. 4 (*b*)). This space-charge region behaves much in the same way as Mott's insulating layer, because of the deficiency of electrons. The effective thickness of the space-charge region will obviously depend on the magnitude and direction of the applied field, and this fits in with the observed changes in the effective capacitance of the rectifier. A summary of Schottky's work has been given by J. Joffé (*Electrical Communications*, **22**, 217, 1945). According to Schottky's views the thickness of the space-charge region is about $10^{-4} - 10^{-5}$ cm., and for a given semi-conductor the height of the barrier, ϕ-χ, naturally depends on the work-function ϕ of the metal. For an excess semi-conductor, the larger ϕ the larger is the reverse resistance of the barrier, and for a defect semi-conductor the best rectification should occur with a metal having a low ϕ. Schottky quoted the result of some measurements to support these predictions, but more recent work (*e.g.* A. V. Joffé, *J. Phys. U.S.S.R.*, **10**, 49, 1946) shows little or no agreement.

In an important recent paper, J. Bardeen (*Phys. Rev.*, **71**, 717, May 15, 1947) examines in greater detail the nature of the contact between a metal and a semi-conductor, and particularly the effects of electronic states in the surface of the semi-conductor. Originally

studied by I. Tamm for a one-dimensional crystal and for a three-dimensional crystal by W. Shockley (*Phys. Rev.*, **56**, 317, 1939), the surface states are shown to lead to levels additional to the impurity levels in the " forbidden " region between the filled and conduction bands of a semi-conductor. The number of the surface-energy states is equal to the number of surface atoms, and half of them are filled in a neutral crystal. There may be, of course, additional localised surface-energy levels arising from surface imperfections, impurities, etc. The surface-energy states may form a continuous distribution if they are sufficiently dense for there to be interaction. Bardeen shows that the surface states with the consequent surface charges may influence considerably the potential distribution near the junction of a metal and a semi-conductor. This would make the potential-barrier height practically independent of the work-function of the metal. A pointer in this direction is given by the results described in a following paper (W. E. Meyerhof, *Phys. Rev.*, **71**, 727, May 15, 1947), which show that in some cases the contact P.D. between a metal and a semi-conductor is not the same as the difference between the work-functions of the two materials measured independently.

The two papers last quoted show that the whole subject of potential barriers at the surfaces of solids needs careful re-examination. There are many additional interesting questions arising from barrier-layer rectification and related phenomena, and some of these may form the subjects of future reviews.

A very useful bibliography of literature on rectifiers and semi-conductors has been published by H. K. Henisch (R.A.E., Farnborough, Jan. 1947).

GENERAL AND PHYSICAL CHEMISTRY.

By J. W. Smith, D.Sc., Ph.D., F.R.I.C., Battersea Polytechnic.

Hydrogen Overpotential.—If a solution of, for instance, sulphuric acid or sodium sulphate is contained in an electrolytic cell with a platinised platinum cathode, and a gradually increasing potential difference is applied to the electrodes, an appreciable current begins to flow and hydrogen is liberated almost as soon as the potential difference between the cathode and the solution attains the value of the reversible hydrogen electrode potential of the solution. With other metals, however, the potential of the electrode has to be made considerably more negative than this reversible potential before appreciable hydrogen evolution occurs. The difference between the reversible hydrogen electrode potential and the potential of a

metal electrode at which hydrogen evolution is occurring is called the hydrogen overvoltage or overpotential at that electrode.

Ever since the first systematic study by Caspari in 1899, the hydrogen overpotential in various solutions and at various electrodes has been the subject of numerous investigations. The reason is not far to seek, since not only is it a matter of great theoretical significance but also of great practical importance. For instance, in the production of hydrogen by electrolysis a high hydrogen overpotential at the cathode means an excessive power consumption, as a higher potential difference must be applied to each cell, and also excessive heat evolution. On the other hand, in certain electrolytic reduction processes much better electrode efficiency is attained at electrodes of high hydrogen overpotential.

Before reviewing the various theories which have been put forward to explain the phenomenon, it is well to consider briefly a few facts regarding it. In early work, Caspari measured the minimum potential at which hydrogen bubble could be formed at a small electrode of the metal now generally known as the "minimum overpotential," whilst Coehn and his collaborators determined the cathode potential, *i.e.* the difference between the potential of the metal and that of a reference electrode in the close proximity of its surface, whilst electrolysis was in progress. The results of the determinations by the two different methods showed, however, only qualitative agreement in indicating for example that the overpotential was low at platinum or iron electrodes but high at lead, zinc, or mercury electrodes.

As early as 1905, Tafel observed that the overpotential increased with increasing current density according to the relationship $I = \alpha e^{\beta\eta}$ or $\eta = a + b \log_{10} I$, where η is the overpotential, I the current density, and α, β, a, and b are constants for any particular metal. Further, for a number of different metals it was found that b had a value of about 0·11. As this corresponds almost exactly to $2{\cdot}3 \times 2RT/F$, where F is the Faraday constant, this relationship has been the main keypoint of the theoretical discussion of the subject. This approach has also been supported by the observation of Bowden (*Proc. Roy. Soc.*, 1929, **A126**, 107) that the value of the constant b increases linearly with the absolute temperature over the range 0° – 72° C.

More recent measurements (Hickling and Salt, *Trans. Faraday Soc.*, 1940, **36**, 1226) have shown that this relationship holds up to current densities at least of the order of 1 amp. per sq. cm. in N–HCl for bismuth, iron, nickel, tungsten, gold, and platinised platinum electrodes, but that at mercury, copper, carbon, cadmium,

tin, aluminium, platinum, rhodium, and lead electrodes deviations occur, the overpotential tending to become constant at high current density.

The value of the constant a in Tafel's relationship, on the other hand, varies very considerably according to the nature of the electrode metal used. Some recent values recorded by Hickling and Salt (*ibid.*, 1942, **38**, 474) are given in Table I.

TABLE I

VALUES OF THE CONSTANT a FOR VARIOUS METAL ELECTRODES

Mercury	1·04	Bismuth	0·69	Iron	0·40	Gold	0·17
Cadmium	0·99	Aluminium	0·58	Nickel	0·33	Rhodium	0·08
Lead	0·91	Copper	0·50	Tungsten	0·27	Platinised platinum	0·01
Tin	0·85	Silver	0·46	Platinum	0·25		

As regards the effect of the nature of the solution used, it was demonstrated by Bowden (*Trans. Faraday Soc.*, 1928, **24**, 473) that the overpotential is independent of the pH value of the solution over the range 6·6 to 0·8, whilst Bethune and Kimball (*J. Chem. Physics*, 1945, **13**, 53) have found that the hydrogen overpotential at a mercury cathode in sulphuric acid solutions is independent of the acid concentration up to about 2·8 M. (24 wt.-% acid). At higher concentrations the latter authors find that the overpotential decreases almost linearly with the wt.-% of the acid present. They bring evidence to show that above this critical concentration the cathodic reaction involves the hydrogen sulphate molecule. In the case of phosphoric acid solutions, the overpotential decreases when the concentration is increased to above 1 M.

Hickling and Salt (*Trans. Faraday Soc.*, 1940, **36**, 1226) have also shown that in the case of the electrolysis of normal solutions of hydrogen chloride in ethylene glycol, ethyl alcohol, and *cyclo*-hexanol, using mercury, tungsten, platinised platinum, tin, and lead cathodes, the overpotential is never less than in aqueous solution and that the positions, shapes, and slopes of the η-log I curves are essentially similar to those for aqueous solutions. This led them to the conclusion that the overpotential is not primarily dependent on the environment of the hydrogen ions. Still more recently, however, Bockris (*Faraday Soc. Symposium*, April 1947) has studied the overpotential of lead, nickel and copper in solutions of hydrogen chloride in methyl alcohol, ethyl alcohol, glycol, formic acid, ether, and acetic acid, and mixtures of most of these solvents with water. He finds that the effect of the solvent depends also on the cathode material. The results for lead and nickel in glycol solutions were in accord with the observations of Hickling and Salt,

but in general the overpotential was found to be lower in pure non-aqueous solvents than in water, and to pass through either a maximum or a minimum at intermediate compositions, the variation from solvent to solvent being least in the case of nickel. The shapes of the η-log I lines were affected by the solvent to a limited extent for all three of the metals.

From the theoretical point of view a metal electrode in equilibrium with a solution containing its ions can be pictured as participating in a dynamic process whereby ions from the electrolyte deposit on the electrode at the same rate as they pass into solution. Under these conditions the electrode attains its reversible potential with respect to the solution and there is no net passage of current. If, however, the electrode is made very slightly more negative with respect to the solution the metal ions must deposit on the electrode more rapidly than they dissolve from it in an endeavour to restore the equilibrium potential and a current will pass, making the metal a cathode. Thus in the case of a copper cathode in neutral copper sulphate solution the electrode needs to be brought to a potential only slightly negative with respect to its reversible potential in order that rapid deposition of copper ions may occur.

The same state of affairs exists in the case of a platinised platinum electrode in a solution containing hydrogen ions, provided the electrode is in contact with gaseous hydrogen. With electrodes of other metals, however, the state of affairs is very different. When a negative potential is applied to such an electrode an initial current surge occurs, but this current drops rapidly and potentials appreciably negative with respect to the reversible value have to be applied before hydrogen is liberated steadily.

Superficially the position is closely analogous to that of a gaseous mixture, such as hydrogen and oxygen at room temperature, which, from the thermodynamic point of view, should combine to form water, but to which extra energy must be supplied in order to overcome an energy hurdle before they can approach the equilibrium state at an appreciable rate.

The process by which a hydrogen ion from the solution becomes a gaseous hydrogen molecule obviously occurs in several stages, and therefore the question arises as to which is the "slow" stage, that is the stage involving the energy hurdle or its equivalent.

If we write the hydrated hydrogen ion arbitrarily as H_3O^+, one series of processes which may be visualised is

(1) Transport of H_3O^+ ions to the vicinity of the electrode.
(2) Detachment of the proton from the water molecule, *i.e.* the reaction $H_3O^+ \rightarrow H_2O + H^+$.

(3) Transfer of H^+ or H_3^+ to the electrode.
(4) Transfer of an electron from the metal to the proton, or less probably to the H_3O^+ ion.
(5) Combination of the hydrogen atoms to form hydrogen molecules.
(6) Evolution of the hydrogen molecules as gas bubbles.

This is by no means the only possible series of processes, and Ferguson and Bandes (*Trans. Electrochem. Soc.*, 1942, **81**, 273) suggested no less than fifteen possible steps, any of which may be slow and this is not necessarily an exhaustive list.

Since the overpotential depends on the nature of the electrode metal rather than on the concentration and character of the electrolyte it is very improbable that step (1) above is the slow stage of the process. On the other hand, each of the other factors mentioned have been suggested as the rate-determining step. Many of the theories lead to a relationship between the overpotential and the current density of the form of the Tafel relationship $\eta = a + b \log I$, and there is what Ferguson (*Faraday Society Symposium*, April 1947) has called "an almost frantic attempt to include something which may be called 'activation,' also to include the expression $RT/\alpha F$ and some sort of a mechanism that will give to α the value 0·5."

The original suggestion of Tafel was that the slow process was the formation of hydrogen molecules from the atoms, this leading to the production of a high concentration of hydrogen atoms and consequently of a high negative potential on the electrode. From free energy considerations the standard potential of atomic hydrogen at one atmosphere pressure should be about 1·9 volts, so that a pressure of 10^{-20} atmosphere would be sufficient to account for the overpotential of a metal such as zinc (about 0·7 volt). On this basis one can attribute the variation in overpotential from metal to metal to the difference in their catalytic activities towards the combination of hydrogen atoms. This view seems to be confirmed by the fact that several metals such as platinum, palladium, and nickel, at which the hydrogen overpotential is low, are also good catalysts for the union of hydrogen atoms and for hydrogenation reactions, in which the dissociation of hydrogen molecules into atoms is probably an intermediate step. Further, it might be inferred that the decrease of overpotential with rise of temperature is due to the increased velocity of combination of the hydrogen atoms.

On the other hand, if it is assumed that the adsorbed hydrogen

atoms occupy only a small fraction of the surface available to them, and that the rate of combination of the atoms is proportional to n^2, where n is the number of adsorbed atoms per sq. cm., the over-potential will be given by $\eta = (RT/F)$ ln. n/n_0, where n_0 is the number of adsorbed atoms per sq. cm. at the reversible potential. For conditions such that n remains constant we obtain, by equating the rates of formation and disappearance of hydrogen atoms the expression $I = kn^2 = kn_0^2 . e^{2\eta F/RT} = I_0e^{2\eta F/RT}$. Alternatively, if account is taken of the fact that the observed current is equal to the rate of combination of hydrogen atoms minus the rate of spontaneous dissociation into atoms, the latter being independent of the potential and equal to I_0, this leads to the expression $I = I_0(e^{2\eta F/RT} - 1)$. It will be noticed that this theory leads to a value of 2 for α in the Tafel relationship, giving

$$\eta = a + (RT/2F) \ln. I = a + 0{\cdot}029 \log I$$

at 18°, whereas the factor b in many cases is 0·11, requiring a value of 0·5 for α. This is the main argument which has been levelled against the theory.

The kinetics of the combination of hydrogen atoms on the electrode was considered in detail by Horiuti and his co-workers (*Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, 1936, **29**, 223). They suggested that, in addition to the direct interaction between adsorbed hydrogen atoms, the removal of the atoms may also occur by an "electrochemical mechanism," *i.e.* by the interaction of a hydrogen atom adsorbed on the electrode and a hydrogen ion from the solution, thus

$$H_3O^+ = H - M + \varepsilon \rightarrow H_2 + H_2O + M.$$

During the last few years this theory has been revived strongly and extended, with various modifications, particularly by Hickling and Ferguson and their co-workers. Thus Hickling and Salt (*Trans. Faraday Soc.*, 1942, **38**, 480) postulate that the discharge of hydrogen ions takes place rapidly to give hydrogen atoms adsorbed on the electrode surface, but that the removal can occur (*a*) by evaporation to give free atomic hydrogen, this taking place to a considerable extent only in the presence of a depolariser; (*b*) by the catalytic combination of two adsorbed hydrogen atoms, and (*c*) at high current density when the available surface is nearly saturated by Horiuti's electrochemical mechanism.

Ferguson and his collaborators take a rather wider viewpoint of the matter. As a result of an oscillographic study of the potential-current curves immediately after the circuit was closed, Ferguson and Bandes (*Trans. Electrochem. Soc.*, 1942, **81**, 273) concluded that

the behaviour observed could be explained on the assumption that the back potential at an electrode was due to the discharge, and thus to the liberation of, an active material at the electrode surface even at the lowest applied potential. The excessive current observed when the current was first closed was attributed to a lack of active material at the electrode, this surge of current liberating active material rapidly until such an amount is formed as to give a back potential practically equal to the applied potential. At the same time the current will decrease to such a value as is required to replace the active material lost by diffusion or otherwise. They infer that the overpotential depends on the activities of atoms and ions at the electrode-solution interface, and that the irregularities which are evident in all types of charge and discharge curves must be due to the factors or forces which determine these activities. In such case the overpotential should be calculable from the activities by the Nernst equation if numerical values for such activities could be obtained.

They suggest that some of the factors and forces which have to be considered in relation to the surface equilibrium are

(*a*) penetration of hydrogen atoms beneath the electrode surface before being discharged ;
(*b*) development of intense pressures below the metal surface ;
(*c*) diffusion of discharged atoms from beneath to the surface, and even into the solution ;
(*d*) adsorption of discharged atoms, ions, and water molecules at the metal surface ;
(*e*) diffusion of atoms along the metal surface ;
(*f*) interfacial forces between the metal, solution, and gas ;
(*g*) orientation of water molecules at the electrode surface, and its alteration with the applied potential ;
(*h*) change in the ion concentration in the really effective solution layer, one or two molecules thick, at the electrode surface due to adsorptive forces, orientation at the electrode, diffusion into and from the body of the solution, electrical conduction, electrical discharge, and the accompanying liberation of the solvent molecules at the electrode surface and a " salting-out " effect due to solvent orientation at the electrode surface.

A completely distinct view of the cause of overpotential, namely that the slow process is the discharge of hydrogen ions, was initiated by Smits in 1922 and developed by Erdey-Gruz and Volmer (*Z. physikal. Chem.*, 1930, **150**, 203). This theory differs from the

last in supposing that the effect is due to the accumulation at the surface of undischarged ions rather than neutral hydrogen atoms. The hydrogen ions which pass to the cathode are regarded as not being discharged at once but, with the electrons of the metal, forming an electric double layer which acts as a condenser, the potential difference across which comprises the overpotential of the electrode. If practically no ions are discharged whilst this double layer is being built up, the potential across the layer will increase proportionately to the total quantity of current passed, as is observed. It is supposed that the condition for an electron to be able to cross the barrier and discharge a hydrogen ion is that the ion and electron between them must acquire a certain activation energy. As the potential of the double layer is increased the potential energy of the doublet is increased and consequently a greater proportion of the ion-electron pairs attain the necessary activation energy, and hence the rate of discharge of hydrogen ions increases. The equilibrium value of the overpotential at any particular current density is therefore that value at which the rate of discharge of the ions across the double layer becomes equal to the rate at which they are transported to the surface.

On the basis of this view it was found possible to derive a relation $\eta = a + (RT/\alpha F)$ ln. I, where α must have a value less than unity. If α is approximately equal to 0·5 this is in accord with observation. The low overpotentials observed with platinised platinum were attributed to the existence of numerous cavities of atomic dimensions in the metal surface, the ions entering these recesses becoming more or less neutralised by the electrons of the surrounding platinum atoms, with which they form dipoles of very small moment, thus producing the behaviour of discharged ions.

This theory has been developed particularly by Frumkin (*Z. physikal. Chem.*, 1933, **A164**, 121; *Acta Physicochim. U.R.S.S.*, 1943, **18**, 23) adopting Stern's theory of the double layer. He supposed the total potential difference between the metal and the solution to comprise two parts, the potential difference (ϕ_h) across the Helmholtz double layer and the potential (ϕ_g) across the diffuse (Gouy) part of the double layer. On this basis the rate of discharge of ions (current) is given by

$$I = k[H^+]_s . e^{\alpha F\phi h/RT}$$

where $[H^+]_s$, the hydrogen ion concentration on the solution side of the Helmholtz double layer, is related to the concentration in the body of the solution $[H^+]_0$ by the relation $[H^+]_s = [H^+]_0 . e^{F\phi g/RT}$.

It follows therefore that

$$\phi_g = (RT/F)\ \ln.\ [H^+]_s - (RT/F)\ \ln.\ [H^+]_o$$

and hence

$$\begin{aligned}\phi_h &= (RT/\alpha F)\ \ln.\ I - (RT/\alpha F)\ \ln.\ [H^+]_s + \text{constant}\\ &= (RT/\alpha F)\ \ln.\ I - (RT/\alpha F)\ \ln.\ [H^+]_o - \phi_g/\alpha + \text{constant.}\end{aligned}$$

The total potential across the double layers is therefore given by

$$\phi = \phi_h + \phi_g = (RT/\alpha F)\ \ln.\ I - (RT/\alpha F)\ \ln.\ [H^+]_o - (1 - \alpha)\phi_g/\alpha + \text{constant.}$$

Since the reversible potential ϕ_o is equal to a constant $-$ (RT/F) ln. $[H^+]_0$, and the overpotential is given by $\eta = \phi - \phi_0$

$$\eta = (RT/\alpha F)\ \ln.\ I - (1 - \alpha)RT/\alpha F\ \ln.\ [H^+]_o - (1 - \alpha)\phi_g/\alpha + \text{constant.}$$

This expression is partially confirmed in a qualitative manner by experiment, but there are a number of observations which are in conflict with it, and considerably more experimental work seems to be required before its implications with regard to the effects of neutral salts on the overpotential, for instance, can be tested completely (Agar, *Faraday Society Symposium*, April 1947).

Other aspects of this theory have also been put forward by various authors, the most distinctive being that of Gurney, who pictured a free atom rather than an adsorbed atom as the product of reaction. He suggested that an energy barrier exists between the electrons in a metal and an ion approaching it, and that, in accordance with the laws of quantum mechanics an electron will only be able to pass through this barrier from a certain electronic energy level to a level of similar energy in the hydrogen ion. Hence, if the energy of an electron in the highest occupied energy level of the metal is less than the energy corresponding to the lowest available electronic level in the hydrated hydrogen ion, no electron can pass from the one to the other and hence the ion cannot be discharged. This state of affairs will hold at absolute zero. At other temperatures a few electrons only will exist in levels which permit transfer, and therefore the latter process will be extremely slow. When a negative potential is applied to the electrode, however, the energies of the electrons are raised until they attain values which permit the transfer to occur. On the basis of this theory Gurney derived an expression of the usual form involving a factor α which, like that in the theory of Erdey-Gruz and Volmer, is approximately constant and less than unity.

The great difficulty with regard to these theories, however, is the explanation of the variation of the factor a in Tafel's relation-

ship with the nature of the cathode material, and with its physical state. In the case of the theories which assume the formation of an adsorbed hydrogen atom it is evident that, since the heat of adsorption of hydrogen atoms varies considerably, this process will be much easier in some cases than in others, with the result that some metals will show much lower overpotentials. In so far as Gurney's theory is concerned, his constant includes a function comprising the energy of the electron in the highest occupied level of the metal and the energy of neutralisation of the hydrated ion, the former of which will vary with the metal concerned. This, however, still does not explain the catalytic properties of metals of low hydrogen overpotential.

In view of the difficulties which are inherent in considering the discharge of an ion by an electron to be a slow process, Eyring, Glasstone and Laidler (*J. Chem. Physics*, 1939, **7**, 1053) developed a theory which supposed the transfer of a proton to be the rate-determining step in the process and hence the cause of hydrogen overpotential. In this theory it is assumed that, in the absence of solutes which are strongly preferentially adsorbed on it, an electrode in an aqueous solution becomes covered to a considerable extent with a unimolecular layer of water molecules. Next to this there will be water molecules associated with the bulk of the solution, and they suggest that the transfer of a proton from a water molecule in the solution to a molecule which is adsorbed on the surface of the electrode is a slow process and is responsible for the overpotential. The proton is then pictured as being discharged immediately by an electron from the metal to form a hydrogen atom, a hydroxyl ion being left in the solution. The whole process can therefore be represented

$$S \ldots H_2O + H_2O \ldots \bar{M} \rightarrow S \ldots OH' + \left.\begin{matrix}H_2O\\H\end{matrix}\right\}M$$

This theory leads directly to a value approximately equal to 2RT/F for the factor b in the Tafel equation. It also suggests that if the metal electrode adsorbs hydrogen strongly, as in the cases of metals such as platinum, palladium, nickel, or copper, relatively stable M—H bonds will be formed and so the proton will pass from the solution layer to the electrode layer more readily than if it only forms weak bonds, as for instance in the case of mercury, and therefore it will have a much lower overpotential. Similarly the metals which form strong bonds to hydrogen atoms will also be good catalysts for the combination of hydrogen atoms to form molecules, but this does not imply that overpotential need be due to the presence of atomic hydrogen. The two phenomena of

low overpotential and high catalytic activity are simply regarded as both being due to the same basic cause, the ease of formation of metal to hydrogen bonds.

The fact that the overpotential builds up linearly with the amount of current passed is explained by supposing that the water molecules on the electrode surface are present as hydrogen and hydroxyl particles, so that whilst the potential is being built up the hydroxyl radicals unite with electrons to form OH′ ions on the surface, thus

$$\left.\begin{matrix}\mathrm{H}\\ \mathrm{HO}\end{matrix}\right\}\overset{-}{\mathrm{M}} \rightarrow \left.\begin{matrix}\mathrm{H}\\ \mathrm{HO'}\end{matrix}\right\}\mathrm{M}.$$

This is regarded as being the only cathode process which takes place before the overpotential is attained, so that the amount of hydroxyl ion formed will be proportional to the quantity of current passed. If these negative ions are balanced by an equal number of positive ions transported by the current from the solution layer to the electrode layer, the potential of the double layer should increase linearly with time.

The application of the theory of absolute reaction rates to the processes concerned, however, led to a function for the specific rate of discharge of ions which involved the total potential of the electrode. The experimental data were found to be in accord with this relationship, however, if the overpotential was substituted for the total potential. To explain this observation the theory was extended by Kimball, Glasstone, and Glassner (*J. Chem. Physics*, 1941, **9**, 91). They postulated the existence of two electrical double layers, with two corresponding energy barriers, at the surface of the electrode. If the barrier nearer the electrode is the higher the overpotential will be essentially established across this layer, whilst the variation of the equilibrium potential caused by changes in the hydrogen ion concentration of the solution is established across the outer double layer. Since the rate of discharge is determined by the potential difference across the inner double layer it is a function of the overpotential rather than of the total potential. The authors point out that both barrier layers may correspond with proton transfer from one water molecule to another or less probably to the discharge process in which a hydrogen atom is formed.

This theory and its extension have been subjected to very severe criticism, however, particularly by Frumkin (*Acta Physicochim. U.R.S.S.*, 1940, **12**, 481) and by Butler (*J. Chem. Physics*, 1941, **9**, 279).

A very different picture of the phenomenon is presented by the

views of Newbery (*Trans. Faraday Soc.*, 1947, **43**, 127). He considers that when hydrogen is being released at a cathode there is formed a condenser, the film of hydrogen gas acting as the dielectric and the metal electrode and the electrolyte, respectively, as the plates. If this film has a thickness equal to the diameter of a hydrogen molecule (about 1·5 A.) its capacity should be 6 μF per sq. cm. This, he points out, is in accord with the observation of Bowden and Rideal (*Proc. Roy. Soc.*, 1928, **A120**, 73) that, when certain electrodes were immersed in dilute acid which had been very thoroughly saturated with hydrogen, 6 micro-coulombs were required to change the potential of 1 sq. cm. by 100 millivolts. He points out that this gas film condenser differs from the double layers postulated by other theories in that the latter would be equivalent in effect to a condenser in parallel with a resistance. Since its action is due to ionic concentrations near the electrode differing from those in the bulk of the solution this arrangement is capable of absorbing electrical energy reversibly by acquiring a state of strain under the influence of an applied E.M.F. As the strain induced by an alternating current will depend in part on the rate at which the ions are displaced, the capacity will vary with the frequency. On the other hand, the capacity of the gas film, as a true condenser in series with the cell circuit, will not vary with frequency. Also, whereas the double layers normally postulated permit free passage of direct current, the gas film will stop the flow of current completely unless the potential applied is sufficient to break through the dielectric.

Newbery's strongest arguments, however, arise from the fact that the Helmholtz type double layer could be produced by any ions, and does not involve the discharge of these ions, whereas the gas film could be produced only after a gas has been liberated on the electrode surface. In this connection he has found that no sudden fall in potential close to the electrode surface can be observed by means of an oscillograph unless a gas is being liberated, copper, silver, lead, or mercury in solutions of their respective salts showing no overpotential. He also found that when his reference electrode was moved away from its normal position in close contact with the experimental electrode, no detectable change could be observed in the potential at low current densities, whilst at higher current density the change could be accounted for fully by the potential drop due to the resistance of the electrolyte. As the space between the capillary and the electrode was about 0·01 mm. or less he considers that it did not leave much room for a diffuse Gouy layer.

His picture of the mechanism of the liberation of hydrogen

involves an initial rush of hydrogen ions to the surface as soon as the potential is applied, the first to arrive being discharged and forming a gas film over the surface. This gas tends to re-ionise and exert a back E.M.F. against the applied potential, but at the same time it forms the very thin dielectric of a condenser. As more ions arrive their discharge is opposed by the gas film and the condenser is charged, great pressure being exerted on the gas film. As the potential gradient across the gas film increases, leakage begins, but every leak is self-sealing so the electrical resistance of the film decreases steadily without any sudden breakdown; at the same time the highly compressed gas is forced into the electrode surface, tending to disintegrate it and destroy any polish. Under the influence of the intense pressure, metallic hydrides are formed which tend to ionise with higher solution pressure than that of hydrogen. Reversible overpotential is therefore attributed to the presence of these overvoltage compounds. The bulk of the gas is supposed to be liberated by the passage of electrons through the gas film, ions thus discharged outside the film aggregating readily to molecules and then to gas bubbles large enough to overcome surface tension forces and escape.

This conflict between various viewpoints is not altogether unexpected if one bears in mind the differences in the characteristics of the metal surfaces at which overpotential phenomena occur. Broadly speaking, metals can be divided into two classes, the metals such as platinum and nickel which adsorb hydrogen strongly, and the others, typified by mercury, which do not adsorb it appreciably. This difference is shown up in the relative ease of liberation of light hydrogen and of deuterium at cathodes of these metals; for the first class of metals the isotope separation factor is about 7, but for the second class it is only about 3.

Some years ago Hammett (*Trans. Faraday Soc.*, 1933, **29**, 770) suggested that the two stages $H^+ + \varepsilon \rightleftharpoons H$ and $2H \rightleftharpoons H_2$ may both be of significance in determining the overpotential, and that the relative importance of the two steps may depend on the nature of the metal surface and the current density. That such a view is necessary to explain all the phenomena associated with the electrode process has been appreciated to a greater and greater extent recently. That there may be a dual mechanism even at the mercury cathode is suggested by the observations of Ganguli (*J. Indian Chem. Soc.*, 1940, **17**, 691), who studied the electrolysis of 0·1 N. sodium sulphate solution containing various concentrations of maleic or fumaric acid, observing the change in cathode potential after switching off the current. When the potential relative to a decinormal calomel

electrode was 1·35 to 1·5 volts immediately after interrupting the current, the potential rose during the first few minutes and then decayed exponentially. On the other hand, when the initial potential was outside these limits it began to decay immediately, as in the absence of reducible material. This behaviour was interpreted as being in accord with the view that both the transference of an electron from the electrode to the hydrated hydrogen ion and the combination of hydrogen atoms adsorbed on the electrode are slow processes with comparable velocities, the combination of these effects accounting for the potential build-up when the current is broken whilst the cathode potential has attained a certain value.

Frumkin (*Acta Physicochim. U.R.S.S.*, 1937, **7**, 475), on the other hand, considers that the difference between mercury and other non-hydrogen-adsorbing metals on the one hand, and nickel and platinum on the other, lies in the slowness in the neutralisation of the ion in the former case, where the proton is rapidly desorbed, as against electrochemical reaction with other metals whereby the proton is transferred from an H_3O^+ ion to an adsorbed hydrogen atom. Horiuti and his co-workers (*Bull. Chem. Soc. Japan*, 1938, **13**, 228), however, have shown by oscillograph methods that the H_2^+ ion exists at the surface of a mercury cathode, so it is evident that the process must be of a relatively complex order.

From this summary it will be appreciated that the whole subject is very complicated, and no theory has yet been put forward which is fully satisfactory in every detail. Such, in fact, is not to be anticipated until much more experimental data has been collected, and the relationship of overpotential to other phenomena more clearly established.

BIOCHEMISTRY.

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The Absorption and Metabolism of Fat

Recent articles in this series have dealt with advances in the field of protein and carbohydrate chemistry. It seems appropriate to devote a few pages to a review of some recent developments which shed light on the fate of fats in the animal organism. We shall deal more particularly with two questions: how is neutral fat absorbed from the alimentary canal? and by what mechanism are the fatty acids oxidised in the tissues of the body? We shall also refer briefly to recent progress in the manufacture of synthetic fats and their possibilities for human nutrition.

Absorption of Neutral Fats from the Alimentary Canal.—During the nineteenth century, the view was widely held that neutral fats were absorbed from the intestine in particulate form without preliminary hydrolysis into fatty acids and glycerol. In the face, however, of apparently conclusive evidence, this view was generally abandoned, and most authorities became convinced that hydrolysis of the fats under the action of pancreatic lipase was a necessary preliminary to absorption from the alimentary tract (see Leathes and Raper, *The Fats*, 2nd edition, 1925, Chap. 6). The relatively small molecules of glycerol and fatty acids were supposed to be readily absorbed through the epithelial cells of the small intestine; within the intestinal wall, resynthesis of the neutral fat from the glycerol and fatty acids was postulated, and this neutral fat, in a finely emulsified form, was transported by way of the lacteals and thoracic duct to the vena cava, where it entered the blood, producing the characteristic opalescence of the plasma which occurs an hour or two after a meal containing fat.

It seemed rather quaint that neutral fat should be completely hydrolysed, only to be resynthesised almost at once. Yet this theory of fat absorption was supported by much experimental evidence, such as that of Frank (*Z. Biol.*, 1898, **36**, 568) that when the ethyl ester of fatty acids was fed to dogs it was the glycerides, and not the ethyl esters, that were found in the thoracic duct; or that of Henriques and Hausen (*Centr. f. Physiol.*, 1900, **14**, 313; *cf.* similar results of Bloor, *J. Biol. Chem.*, 1913, **15**, 105), who administered a mixture of lard and vaseline to rats and found that the lard was mostly absorbed, but the vaseline was almost completely excreted in the fæces.

During the past ten years the whole question has been reopened by the work of Frazer and his colleagues. (For a recent summary see Frazer, *Chem. and Ind.*, 1947, 379; also *Physiol. Rev.*, 1946, **26**, 103). Frazer (*Analyst*, 1938, **63**, 308; *J. Physiol.*, 1943, **102**, 306, 329) found evidence that the absorption of olive oil on the one hand, and of a mixture of glycerol (1 mol.) and oleic acid (3 mol.) on the other, from the intestines of rats took place by different routes. After administration of olive oil, fat globules appeared in relatively large numbers in the systemic blood, with few in the portal blood; with a mixture of glycerol and oleic acid, the opposite was found. Further, if the lipoid material was stained with Sudan IV, the depot fats contained the dye in the former case, and the liver fats in the latter. These results strongly suggested that neutral fats, *e.g.* olive oil, are absorbed through the lacteals and the thoracic duct, so passing directly into the blood-stream and on to the fat

depots, whilst the mixture of glycerol and fatty acids appears as fat in the portal vein and so passes into the liver. When the olive oil was administered along with a plentiful supply of lipase, the absorption proceeded very much the same as with the mixture of glycerol and oleic acid. The high concentration of lipase might be expected to effect hydrolysis of the fat very rapidly and so cause it to be absorbed like a mixture of oleic acid and glycerol. The implication is that, under normal conditions, neutral fats are not completely hydrolysed, but that unhydrolysed fat is capable of being absorbed into the lacteals.

Frazer and his co-workers adopted the hypothesis that the essential condition for the absorption of fat from the intestine is that it should be very effectively emulsified. After the administration of olive oil, the fatty particles in the intestinal canal of the rat were found to have a diameter of less that $0{\cdot}5\,\mu$. The failure of non-hydrolysable fat-like substances, such as paraffin, to be absorbed from the intestine was one of the facts which seemed to support the orthodox view. However, Frazer found that the particles of paraffin administered to a rat did not normally fall below $10\,\mu$ in the intestine, and it is not surprising that these large particles fail to be absorbed. If the paraffin was deliberately emulsified before administration, so that the particles were much smaller, absorption did take place; the smaller the particles the greater the degree of absorption. When the diameter of the particles was of the order of $0{\cdot}5\,\mu$, the absorption in six hours was about 40 per cent., a figure comparable with that obtained with olive oil under similar conditions.

If fat can be absorbed without hydrolysis, what then is the function of the lipases in the intestinal tract? Frazer's view is that the lipase promotes the emulsification of the fat. This it does by acting on some of the fat to form substances aiding in this emulsification. Much light is shed on this point by experiments reported in two recent papers.

In one paper (Frazer, Schulman and Stewart, *J. Physiol.*, 1944, **103**, 306) the power of various substances and combination of substances to promote the emulsification of neutral fats was investigated. The substances they used were: soap (sodium oleate), cholesterol, bile salts and monoglyceride (glycerol with one hydroxyl group esterified with fatty acid). Experiments were carried out at different *p*H values, and in estimating emulsifying power the criteria used were: smallness of particles, spontaneity of emulsification and stability of emulsion. It was found that to bring about efficient emulsification soap must be present. If this were present, its emulsifying power was increased substantially by monoglyceride;

without bile salts, even a combination of monoglyceride and soap was of little use, unless the pH was above 7. The addition of bile salts made the emulsifying power almost independent of the pH over a wide range, and such mixtures, containing soap, monoglyceride and bile salts, emulsified well, even on the acid side of neutrality. Cholesterol did not seem to have any significant effect.

In another paper, Frazer and Sammons (*Biochem. J.*, 1945, **39**, 122) examined the action of pancreatic lipase on olive oil under a variety of conditions. Bile acids were added to promote emulsification, and the pH was varied from 6 to 10·5. The most striking result was that, though in the first four hours considerable quantities of free fatty acid appeared (up to about one-third of the maximum theoretically possible), no trace of glycerol could be detected. Control experiments showed that the conditions were not such as to destroy added glycerol. After forty-eight hours, the amount of free fatty acid had risen to fully one-half of the maximum and the amount of liberated glycerol was comparatively small. Analysis of the reaction mixture proved that considerable quantities of mono- and di-glycerides were present. The conclusion drawn is that lipase readily splits off one, and even two fatty acid molecules from a neutral fat, but that it removes the third fatty acid only very slowly. In the few hours during which fat is submitted to lipase action in the small intestine, at most only traces of free glycerol can be formed.

It is perhaps surprising that this important circumstance should not have been recognised earlier. Some observations bearing on the point were made by Terroine (*Biochem. Z.*, 1910, **23**, 404), who found that pancreatic lipase, acting on triacetin and tributyrin (the glycerides of acetic and butyric acid respectively) removed the first acyl group readily, the second more slowly, and the third very slowly indeed. This early clue does not seem to have been followed up, and it is not clear from Frazer's papers whether he was aware of these results of Terroine. It appears to be an example of some highly significant facts being discovered, then lapsing into obscurity, to be rediscovered independently a generation later.

Frazer and his co-workers, then, seem to have made out a strong case for discarding the view held generally twenty years ago, and for believing that a considerable proportion of the fat taken by mouth is absorbed without hydrolysis. Some hydrolysis admittedly takes place, but the products of this hydrolysis, besides fatty acids, are mono- and di-glycerides; little, if any, glycerol seems to be formed in the small intestine under the conditions of normal digestion. The finely emulsified, unhydrolysed fats are absorbed into

the lacteals and pass to the thoracic duct ; free fatty acid is mainly taken up into the portal system. The authors have confirmed and elaborated this general picture by many observations, biochemical, physiological and histological, for which the original papers must be consulted. The wheel has turned full circle, and we have reverted to a view not very different from that commonly held fifty years ago. We have still to reckon with some of the experimental findings which previously led to the rejection of this theory, for example the observations of Henriques and Hausen on the preferential absorption of lard from a vaseline-lard mixture administered to rats. Further work is evidently required before the problem can be regarded as finally solved, but meanwhile, though all difficulties have not yet been removed, the evidence presented by Frazer and his colleagues seems cogent and convincing.

Intermediate Metabolism of Fatty Acids.—We are still in much ignorance as to the exact steps by which fatty acids are oxidised in the animal body, and in particular as to how the energy liberated in this oxidation is transformed into mechanical work. During the past decade, a new method has become available for tackling these and similar problems of metabolism ; by using isotopic hydrogen, or carbon, or nitrogen, it is possible to "label" specific atoms in a molecule, and with the help of this label to follow the one particular atom through its metabolic career. This powerful method has made it possible to tackle problems which previously seemed too difficult to be soluble, and already a flood of light has been cast on many obscure questions. For an account of methods used and the results of earlier work, Schoenheimer's well-known book, *The Dynamic State of Body Constituents* (Harvard University Press, 1942), may be consulted.

Weinhouse, Medes and Floyd have used labelled carbon (carbon with an excess of ^{13}C) to investigate the mechanism of oxidation of fatty acids in animal tissues. The fatty acids found in nature are in general straight-chain fatty acids, containing an even number of carbon atoms. It is known that oxidation of such acids *in vitro* by liver slices leads to the formation of acetoacetic acid, $CH_3CO.CH_2CO_2H$. As this acid also appears in the blood and urine of animals and man during starvation, as well as in certain pathological conditions such as diabetes, it is generally regarded as a product of the oxidation of fatty acids ; normally it is apparently further metabolised and so does not accumulate. It was suggested by Knoop that fatty acids in the body undergo β-oxidation. This means that the carbon atom next but one to the carboxyl group is oxidised ; a fatty-acid molecule two carbon atoms shorter than

the original one is produced, and a two-carbon atom fragment is set free. A simple and plausible assumption is that the two-atom fragment takes the form of acetic acid. According to this view, any fatty acid with an even number of carbon atoms greater than four is broken down to butyric acid, $CH_3CH_2CH_2CO_2H$, in successive steps, two carbon atoms being lost at each step. The butyric acid then undergoes further β-oxidation, with the result that acetoacetic acid is formed. On this theory, the carbon atoms of the acetoacetic acid are the four terminal carbon atoms of the original fatty acid, furthest from the carboxyl group.

An alternative view of the genesis of acetoacetic acid is possible. This view is also based on the idea of β-oxidation. We may imagine that the whole of the fatty acid is oxidised in steps with the formation of acetic acid, and that some of the acetic acid is resynthesised by random combination of pairs of molecules into acetoacetic acid

$$2CH_3CO_2H = CH_3COCH_2CO_2H + H_2O$$

A third view has been suggested by Hurtley (*Quart. J. Med.*, 1915–16, **9**, 301) and supported by Jowett and Quastel (*Biochem. J.*, 1935, **29**, 2159), according to which oxidation takes place more or less simultaneously at alternate carbon atoms, followed by random fission throughout the chain, thus:

$$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—COOH$$
$$\downarrow$$
$$CH_3—CO—CH_2—CO—CH_2—CO—CH_2—COOH$$
$$\downarrow$$
$$2CH_3—CO—CH_2—COOH$$

or

$$CH_3—CO—CH_2—COOH + 2CH_3COOH$$

In order to decide between these three theories, Weinhouse, Medes and Floyd (*J. Biol. Chem.*, 1944, **153**, 689; 1944, **155**, 143; 1945, **157**, 35) prepared *n*-octanoic acid, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CO_2H$, in which the carbon of the carboxyl group was labelled by containing an excess of ^{13}C. This acid was oxidised in presence of rat-liver slices, and the resulting acetoacetic acid collected and examined. The acetoacetic acid was found to contain some labelled C; this labelled C was located wholly in the carboxyl and the CO— group, there being none in the CH_3— or —CH_2— groups. The excess of ^{13}C in the carbon of the —CO— group was, within experimental error, the same as that in the carboxyl carbon. It will be seen at once that these results are at variance with the requirements of the first theory, as to the mechanism of acetoacetic acid formation; for, according to it, the four carbon atoms in the acetoacetic acid represent the

four terminal carbon atoms of the original fatty acid, and so should contain no labelled carbon. They are also at variance with the third theory; for, according to it, only the carboxyl group of the acetoacetic acid could be derived from the carboxyl group of the fatty acid, and the —CO— group could not contain labelled carbon.

The experimental results, in fact, show that the labelled carboxyl group, present in the octanoic acid, contributes just as much to the —CO— group as to the carboxyl group of the derived acetoacetic acid. These findings are in complete harmony with the second theory, according to which the acetoacetic acid is formed by random recombination of the acetic acid molecules produced during the β-oxidation of the fatty acid. Any acetic acid molecule containing labelled carbon in the carboxyl group has equal chances of combining so that the labelled carbon is in the carboxyl group or in the —CO— of the resulting acetoacetic acid. Thus the excess of ^{13}C in these two positions should be equal.

When n-butyric acid containing labelled carbon in the carboxyl group was employed in the experiments instead of n-octanoic acid, rather more of the labelled carbon was found in the carboxyl group of the resulting acetoacetic acid than in the —CO— group. This suggests that here some of the acetoacetic acid might be derived directly by oxidation of the butyric acid, without intermediate formation of acetic acid. The quantitative results, however, indicate that the greater part of the acetoacetic acid, in this case too, is formed indirectly, with acetic acid as intermediary.

It is clearly relevant to enquire whether it can be demonstrated that acetic acid is, in fact, converted into acetoacetic acid in presence of rat-liver slices. That it is has been shown conclusively by Weinhouse, Medes and Floyd (*J. Biol. Chem.*, 1945, **158**, 411), who, following their usual technique, used acetic acid labelled with ^{13}C in the carboxyl group, and found that the acetoacetic acid produced contained the labelled C in both the —CO— and carboxyl groups, in approximately equal amounts. A similar production of acetoacetic acid from acetic acid, but in the intact animal, had previously been demonstrated by Swengseid, Barnes, Hemingway and Nier (*J. Biol. Chem.*, 1942, **142**, 47).

One effect of the work of Weinhouse, Medes and Floyd is to emphasise the importance of acetic acid in fat breakdown. It suggests, too, that acetic acid may be important in connection with the synthesis of fatty acids in the body. It condenses to acetoacetic acid; on reduction this would give butyric acid. By the further condensation of acetic acid molecules, followed by reduction, the fatty acid chain may be lengthened, and in this

way the synthesis of the even-numbered higher fatty acids might be achieved. That such synthesis does in fact take place is borne out by the experiments of Rittenberg and Bloch (*J. Biol. Chem.*, 1945, **160**, 417) with acetic acid containing labelled carbon and hydrogen. Animals fed with acetate so labelled are found to contain labelled carbon and hydrogen in their body fatty acids. This indicates that the fatty acid has, in part at least, been formed from the administered acetate.

It is not only in fatty acid metabolism that acetic acid may be important. Experiments with labelled acetic acid (Rittenberg and Bloch, *loc. cit.*) have indicated that this compound takes part in the synthesis of cholesterol in the animal body. Furthermore, there is evidence that acetic acid is readily formed in the breakdown of glucose; pyruvic acid and its phosphate is a well-known product of normal glycolysis, and these compounds undergo oxidative decarboxylation with the formation of acetic acid or acetylphosphate. The latter is a compound of high chemical activity, with an energy-rich phosphate bond, and it may be in this form that acetic acid often acts in its rôle as a synthetic intermediary.

Acetic acid, then, is an obvious link between carbohydrate and fat metabolism. It has also relations with the metabolism of certain aminoacids, and so it links up with protein metabolism as well. In fact, a minor revolution in biochemistry seems to be taking place, which is singling out acetic acid as a key compound in metabolic processes; only a few years ago, it seemed doubtful whether this acid had any significance at all in animal metabolism.

SYNTHETIC FATS.—An interesting account has appeared (*Chem. and Ind.*, 1947, p. 251) of the progress made, especially in Germany, during recent years, in the preparation of synthetic fats. In the process used for large-scale production, the starting material was a hydrocarbon fraction, b.p. 320°–450°, known as "gatsche," obtained from the oil produced by the well-known Fischer-Tropsche method from coal through the intermediary of water-gas. This gatsche is oxidised by air at 105° in presence of permanganate as a catalyst. The hydrocarbons are oxidised to fatty acids, hydroxy-fatty acids and a number of other products. It is necessary to interrupt the reaction while a large proportion of the oil is unattacked, otherwise the fatty acids formed are themselves oxidised, and the yield of fatty acids reduced. The recovered gatsche can be used in succeeding batches. The fatty acids are separated and purified by a somewhat elaborate process; they are finally fractionated so as to obtain the C_{10}–C_{20} acids. The product contains all these acids, odd as well as even members of the series, in roughly equal amounts.

For the actual preparation of the synthetic fat, the synthetic fatty acids are treated with glycerol in a vacuum, in presence of tin or zinc as a catalyst. The resulting fat is refined, and may then be converted into a margarine-like material by compounding with water, salt, diacetyl and carotin concentrates, and emulsifying the mixture. The cost of the preparation of synthetic fat is high; it seems that, under normal conditions, there is no chance of its competing with natural fats.

A considerable amount of work has been done on the nutritive value of synthetic fat, but the results so far are not altogether conclusive. From the chemical point of view, the essential difference between the synthetic and natural fats is that the latter contain only fatty acids with an even number of carbon atoms, whilst the former contain the odd as well as the even acids. On the whole, the evidence suggests that the odd fatty acids are metabolised by the animal organism just as well as the naturally occurring even ones. This is what would be expected if the fatty acids were broken down by β-oxidation, with the formation of acetic acid. There is no obvious reason why the odd members of the series should not undergo β-oxidation just as well as the even ones. There is some evidence, too, that triglycerides containing the odd acids are just as readily attacked by lipase as are the normal fats. On the other hand, when the synthetic fats are actually administered to man or animals, it would seem that they are not quite so well absorbed from the intestinal tract. If this proves to be a significant observation, it may be due to differences in physical rather than chemical properties; for example, to less facile emulsification. The natural fats are usually associated with non-fatty products, for example, traces of protein, which may modify their physical properties.

These synthetic fats were used for human consumption in Germany during the war. They were produced in quantities which, although small in comparison with the total fat consumption of the country, were not inconsiderable in an absolute sense (up to 2000 tons per year). They were supposed to have especially good keeping properties, and so were earmarked for the use of submarine crews, and for soldiers on the African campaign. However, the palatability of most, if not all, synthetic fats so far produced seems to have been distinctly inferior to that of the natural fats ordinarily used for human consumption, and this, along with their high price, seems to rule them out of account for normal human nutrition, at least for a long time to come.

GEOLOGY. By G. W. Tyrrell, A.R.C.Sc., D.Sc., F.R.S.E., The University, Glasgow.

Stratigraphical and Regional Geology.—"The Great Glen Fault," described and re-interpreted by W. Q. Kennedy (*Quart. Journ. Geol. Soc.*, CII, Pt. 1, 1946, 41–76), is the great dislocation which intersects Scotland along the remarkably straight feature which runs from Loch Linnhe to Inverness. It has been interpreted as a normal or dip-slip fault with downthrow to the south-east. Professor Kennedy, however, gives strong evidence that it is a lateral-slip or wrench-fault with a horizontal displacement of about 65 miles. The main evidence for this startling conclusion is the displacement of certain geological features, *e.g.* the great belt of regional injection which affects the Moine Schists of the Northern and Grampian Highlands, and the Strontian Granite. The latter is truncated, but the missing southern portion can be identified as the Foyers Mass, 65 miles to the north-east and similarly truncated by the fault.

An important memoir by J. G. C. Anderson on "The Geology of the Highland Border: Stonehaven to Arran" (*Trans. Roy. Soc. Edin.*, LXI, Pt. II, 1947, 479–515) revolutionises, on what appears to be good evidence, our ideas on the structure and succession within that complex belt, the Highland Border Fracture-zone, which runs for 160 miles in a north-easterly direction from Arran to Stonehaven. The old omnibus term, the Highland Border Series, is extinguished, and the rocks formerly assigned to it are re-distributed between the Dalradian (boldly labelled Cambrian) and Ordovician (Arenig spilites, black shales and cherts; post-Arenig breccias, conglomerates, grits and limestones). The Leny Grits and the Ben Ledi Grits, formerly separated, are now shown to be one and the same formation. The Cambrian and Ordovician rocks have been thrown by the Caledonian orogeny into closely packed folds which are commonly overturned towards the south-east. The rocks have been affected by the regional metamorphism of the Scottish Highlands in general. As this metamorphism does not affect the Lower Old Red Sandstone sediments and lavas along the Highland Boundary Fault, it is of Lower Palæozoic age.

"The Kinlochlaggan Syncline, Southern Inverness-shire," described by J. G. C. Anderson (*Trans. Geol. Soc. Glasgow*, XXI, Pt. I, 1947, 97–115), presents a major fold traceable in a north-north-easterly direction for 20 miles. In upward succession the strata involved are granulites of Moine age, pelitic schists, the Kinlochlaggan Quartzite and the Kinlochlaggan Limestone Group. The last-named is

Dalradian and probably equivalent to the Ballachulish Limestone. The ages of the pelitic schist and quartzite are doubtful and their correlation is left for future research.

In a paper on "Loch Awe Succession and Tectonics: Kilmartin-Tayvallich-Danna," A. Allison (*Quart. Journ. Geol. Soc.*, XCVI, 1941, 423–50) has established two series of strata, the Crinan Grit Group and the Tayvallich Limestone Group, of which the latter is the younger. The Crinan Grit Group is composed of quartzo-feldspathic grits with two important limestone-slate intercalations in its upper part. It is injected by epidiorite sills and the grits show graded but not current bedding. The Tayvallich Limestone Group is composed of dark gritty limestones, vesicular epidiorites including undoubted pillow-lavas, and breccias or conglomerates of epidioritic material. The rocks are compressed into small open folds with steep but not inverted limbs facing the west-north-west.

A great dislocation associated with the Tertiary igneous rocks of Rhum was described by Harker in 1903 as an overthrust of Early Palæozoic age. It is now claimed as a Tertiary ring fault with central uplift by E. B. Bailey in a paper entitled: "Tertiary Igneous Tectonics of Rhum (Inner Hebrides)" (*Quart. Journ. Geol. Soc.*, C, 1945, 165–91). The feature interpreted by Harker as a tectonic breccia in the Torridonian is now regarded as slump-bedding; and what Harker thought was crushed Torridonian overlying transported Durness Limestone is now regarded as a patch of Trias with a basal cornstone.

The associated gneisses which Harker interpreted as banded Tertiary intrusions are now restored to the Lewisian to which they were originally assigned by A. Geikie. The outstanding tectonic structure of Rhum is a block uplift approaching a maximum of 7000 ft. which took place at the beginning of the Tertiary vulcanicity. The peridotites of the island were later than the uplift, and rose along ring fissures centred to the west of the great initial ring fault.

A study of Harker's original specimens by C. E. Tilley in a "Note on the Gneisses of Rum," (*Geol. Mag.*, LXXXI, 1944, 29–32) confirms Bailey's views as to their age. Some of the gneisses are thermally metamorphosed adjacent to a contact with eucrite.

"The Dalradian Rocks of Arran," investigated by J. G. C. Anderson (*Trans. Geol. Soc. Glasgow*, XX, Pt. III, 1944, 264–86) can readily be assigned to two groups, the Loch Ranza Slates and the North Sannox Grits. The latter form a continuous section 6200 ft. thick, and are younger than the Slates which form the core of a great fold—the Loch Ranza Anticline—both limbs of which dip

steeply to the south-east. The Loch Ranza Slates are correlated with those of Dunoon and Aberfoyle and the North Sannox Grits with the Leny and Ben Ledi Grits.

In a paper on "The Arenig Rocks of Arran and their Relationship to the Dalradian Series," J. G. C. Anderson and J. Pringle (*Geol. Mag.*, LXXXI, 1944, 81–8) reaffirm the Arenig age of the rocks both on the evidence of fossil fragments, and on their close resemblances to the Arenig of Ayrshire and Aberfoyle. The Arran exposures outcrop between two bands of Dalradian grits in North Glen Sannox. The evidence of graded bedding suggest that the grits on the west present a younger side to the Arenig, and seem to have been the floor on which the latter were deposited. The grits on the eastern side are brought up by a fault.

O. Holtedahl, in "Correlation Notes on Scottish-Norwegian Caledonian Geology" (*Norsk Geol. Tidsskr.*, **19**, 1939, 326–39), discusses some structural features which favour correlation of the Moine Gneiss of Scotland with the metamorphic Sparagmitian (Eo-Cambrian) of Scandinavia, and possibly of the Torridonian with the non-metamorphic pre-tillite Sparagmite. The Scottish Islay-Schichallion boulder-bed is correlated with the tillites of the Upper Sparagmitian, and the higher Dalradian with the lower Cambro-Silurian of the Scandinavian Caledonian zone.

The main object of O. Holtedahl's memoir "On the Caledonides of Norway" (*Norske Vidensk.-Akad. Oslo, I. Math.-Nat. Kl.*, 1944, No. 4, 31 pp.) is to link up the southern and northern parts of the elongated Caledonian belt of Norway in one general structural scheme. A marked characteristic of the Caledonides of Norway is the movement of enormous plutonic masses (*e.g.* the Bergen-Jotun group of Goldschmidt) for very long distances horizontally, and on the whole above metamorphosed and folded Cambro-Silurian sediments. The "roots" of these igneous masses must be sought in far north-western regions, the magmas rising from depth or produced *in situ* by palingenetic processes. This work is so full of detail as to defy summary, but there is an extremely valuable geological map which greatly aids elucidation.

The important large quarto memoir on the "Geology of the Bergen Arc System," by the late C. F. Kolderup and his son N. H. Kolderup (*Bergens Mus. Skrifter*, No. 20, 1940, 137 pp.), has only recently come to hand. It is impossible to summarise this major work in a short paragraph. The Bergen Arcs are three in number; two belts, an Outer or Major, and an Inner or Minor, consist of Cambro-Silurian schists the outcrops of which form semi-circles open or concave to the west. A third arc consisting of igneous rocks

of the anorthosite kindred intervenes between the two Cambro-Silurian arcs. The memoir deals successively with the Palæozoic Arcs and their intrusive rocks; the Anorthosite Kindred (a most valuable section for petrologists); the Migmatitic Gneisses, etc., which border the major arc to the east, and form the central part of the whole system; and finally the tectonics. The arc structure, dominant in the west, fades out to the east and north-east; it is thought to be due to movements originating in the west. But a full explanation of the tectonics of West Norway must await investigation of the little-known gneiss areas between Bergen and Trondheim.

The Tiirismaa Quartzite described by P. Eskola and E. Nieminen in their paper on "The Quartzite Area of Tiirismaa near Lahti" (*C.R. Soc. Géol. de Finlande*, No. 12, 1938, 30–45) is early Archæan in age, certainly older than Sederholm's second granite, and probably older than his first, the earliest of the Sveco-Fennian orogeneses. Hence it must be one of the most ancient sedimentary formations in the world.

W. D. Evans describes "The Geology of the Prescelly Hills, North Pembrokeshire" (*Quart. Journ. Geol. Soc.*, CI, 1945, 89–110). The rocks range from the Arenig to the Bala, the main formations being the Sealyham Volcanic Series (rhyolites and tuffs in the west; trachytes in the east); the *Didymograptus bifidus* shales and mudstones; the Fishguard Volcanic Series (brecciated and spherulitic rhyolites with tuffs and ashy shales). Sills of quartz-dolerite and a keratophyre cut the Arenig and Llanvirn, but do not penetrate into higher strata. The rocks have a Caledonoid strike and are disposed about two eastwardly pitching anticlines and a complementary syncline which are broken by faults and overthrusts.

C. A. Matley and T. C. Wilson describe "The Harlech Dome, north of the Barmouth Estuary" (*Quart. Journ. Geol. Soc.*, CII, Pt. 1, 1946, 1–40). It contains some 10,000 ft. of Cambrian rocks (Lower Cambrian to Ffestiniog Flags) with thick grit formations. They are intruded by Lower Palæozoic greenstones of more than one age. The sediments, the petrology of which is described by A. W. Woodland, have undergone low-grade metamorphism. The general structure is a broken anticlinorium which has been compressed from west to east, cleaved in a northerly direction and intersected by numerous large faults.

Other recent papers on Welsh stratigraphy are: W. G. Fearnsides and W. Davies, "The Geology of Dendraeth. The Country between Traeth Mawr and Traeth Bâch, Merioneth" (*Quart. Journ. Geol. Soc.*, XCIX, Pts. 3 and 4, 1944, 247–76); E. Greenly, "The Arvonian Rocks of Arvon" (*ibid.*, C, Pts. 3 and 4, 1945, 259–88); W. D. V.

Jones, "The Valentian Succession around Llanidloes, Montgomeryshire" (*ibid.*, 309–32).

Discussing "The Periods of Coal Formation represented in the British Coal Measures," A. E. Trueman (*Geol. Mag.*, LXXVIII, 1941, 71–6) says that the most striking feature in the distribution of British Carboniferous coals is the widespread occurrence of important seams in practically all the coalfields in the Ovalis and Modiolaris Zones and the lower part of the Similis-Pulchra Zone. Before this period there had been local episodes of coal formation in certain northern areas, but there was no gradual southward transgression of the "Coal Measure" facies. Rather, it may be said that the Upper Carboniferous (Ammanian) episode began in the Yorkshire–Lancashire area, and extended thence both to more northerly and more southerly localities.

T. N. George has analysed "The Structure of Gower" (*Quart. Journ. Geol. Soc.*, XCVI, 1940, 131–98), that remnant of the Armorican fold system between Swansea and Carmarthen Bays. The solid geology is almost wholly Upper Palæozoic. The main structure is that of a series of more or less east-and-west folds arranged *in echelon*; but the successive replacements of fold axes are rarely simple. They often coincide with large transverse fractures of variable and differential throw which are of the nature of tear or strike-slip faults. These have grown as horizontal shearing dislocations concomitantly with the folds as elements in a single process. The tectonic plan of Gower may be interpreted as due to tangential compressive stresses in a north-north-easterly direction, causing folds along lines normal to the direction of pressure, and tear faults in that direction.

Other papers on the geology of the South Wales Carboniferous are: L. R. Moore and A. H. Cox, "The Coal Measure Sequence of the Taff Valley and its Correlation with the Rhondda" (*Proc. S. Wales Inst. Eng.*, LIX, No. 2, 1943, 189–304); L. R. Moore, "The Geological Sequence of the South Wales Coalfield: The 'South Crop' and Caerphilly Basin, and its Correlation with the Taff Valley Sequence" (*ibid.*, LX, No. 3, 1945, 141–252).

In their paper on "The Bristol and Somerset Coalfields with Particular Reference to the Prospects of Future Development," L. R. Moore and A. E. Trueman (*Proc. S. Wales Inst. Eng.*, LVII, No. 3, 1942, 180–247; 303–5) show that the geological history of the Bristol area has been very similar to that of South Wales, and the sequence of strata is much the same. The Palæozoic rocks of the area are highly disturbed by intense folding due to pressures from the south and east; numerous overthrusts, including the

famous "Radstock Overlap Fault," have been produced; and steeply inclined faults trending approximately at right-angles to the fold lines, are important. As regards prospects it is known that only a small fraction of coal from the Lower Coal Series has been mined, and considerable areas await development; but the outlook for further extensive mining in the Upper Coal Series is uncertain.

Other recent papers dealing with Upper Palæozoic rocks in the United Kingdom are: D. Parkinson, "The Origin and Structure of the Lower Viséan Reef-knolls of the Clitheroe District, Lancashire" (*Quart. Journ. Geol. Soc.*, XCIX, Pts. 3 and 4, 1944, 155–68); K. C. Dunham and C. J. Stubblefield, "The Stratigraphy, Structure and Mineralization of the Greenhow Mining Area, Yorkshire" (*ibid.*, C, Pts. 3 and 4, 1945, 209–68); J. Shirley and E. L. Horsfield, "The Structure and Ore-deposits of the Carboniferous Limestone of the Eyam District, Derbyshire" (*ibid.*, 289–308); R. G. S. Hudson and G. Cotton, "The Carboniferous Rocks of the Edale Anticline, Derbyshire" (*ibid.* CI, Pts. 1 and 2, 1945, 1–36); F. W. Cope, "Intraformational Contorted Rocks in the Upper Carboniferous of the Southern Pennines" (*ibid.*, CI, Pts. 3 and 4, 1946, 139–76).

G. M. Lees and A. N. Taitt have described "The Geological Results of the Search for Oilfields in Great Britain" (*Quart. Journ. Geol. Soc.*, CI, 1946, 255–317). Their own concise summary is here transcribed: "The search for oil in Great Britain has been carried out in five separate geological provinces—in the Mesozoic of southern England, the Carboniferous of the eastern Midlands, the Triassic and Carboniferous of Lancashire, the Permian of North Yorkshire, and the Calciferous Sandstone Series of the Midland Valley of Scotland. Four oilfields have been discovered in Nottinghamshire and a small field in Lancashire. In addition, a large amount of new stratigraphical information has been provided by the exploration borings and extensive geophysical surveys have added considerably to existing knowledge of the structure of the Carboniferous in the eastern Midlands. The boring records have given much new information on the development of coal seams in the areas east and south-east of the present Nottinghamshire Coalfield. A boring in North Yorkshire proved the presence of potash salts in the Permian indicating conditions comparable with those of North-West Germany."

The following are valuable accounts of the geology of certain British oilfields: H. M. Sale and P. Evans, "The Geology of British Oilfields. I. The Geology of the Assam-Arakan Oil Region (India and Burma)" (*Geol. Mag.*, LXXVII, 1940, 337–63); G. S. Hume, "II. The Geology of the Oilfields and some Prospective Oil Areas

in Canada" (*ibid.*, LXXVIII, 1941, 1–36); P. Evans and C. A. Sansom, "III. The Oilfields of Burma" (*ibid.*, 321–50).

The "Outlines" of the geology of restricted regions or countries which are published from time to time are of great value for students of general geology and also of more specialised parts of the subject. For instance, the writer, who is interested in the distribution of igneous rocks in time and space, finds these accounts of considerable help in providing the geological background for "petrographical provinces." They are, of course, mainly compilations, but they are frequently supplemented with the latest original work by the authors concerned. The following are some recent papers on these lines: A compilation "Geology of Eastern Iran" by F. G. Clapp (*Bull. Geol. Soc. Amer.*, 51, 1940, 1–102) includes much new reconnaissance work on a little-known area by a group of American oil geologists. The rocks range from Pre-Cambrian to Recent, but Ordovician and Silurian rocks are unknown. The maximum collective thickness of the sediments is nearly 100,000 ft.

Sir Douglas Mawson has written a valuable conspectus of South Australian geology in two papers: "Progress in Knowledge of the Geology of South Australia" (*Trans. Roy. Soc. S. Austr.*, LX, 1936, lvi–lxv) and "The Geological Background of South Australia" (*Handbook of 25th Meeting of the Australian and New Zealand Assoc. Adv. Sci.*, Adelaide, 1946, 5–11). Three further papers continue his work on the Cambrian and Pre-Cambrian of the state: "The Most Northerly Occurrence of Fossiliferous Cambrian Strata yet recorded in South Australia" (*Trans. Roy. Soc. S. Austr.*, LXI, 1937, 181–6); "Cambrian and Sub-Cambrian Formations at Parachilna Gorge" (*ibid.*, LXII, 1938, 255–62); "The Mount Caernarvon Series of Proterozoic Age" (*ibid.*, 347–51). For Queensland we have: W. H. Bryan and O. A. Jones, "The Geological History of Queensland . . . A Stratigraphical Outline" (*Univ. of Queensland Papers*, II (N.S.), No. 12, 1946, 103 pp.).

Recent work in New Zealand includes the following: H. J. Finlay and J. Warwick, "The Divisions of the Upper Cretaceous and Tertiary in New Zealand" (*Trans. Roy. Soc. N.Z.*, 70, Pt. 1, 1940, 77–135); E. O. Macpherson, "An Outline of Late Cretaceous and Tertiary Diastrophism in New Zealand" (*N.Z. Dept. Sci. Indus. Res. Geol. Mem. No. 6*, 1946, 32 pp.); J. Warwick, "The Geology of the Te Kuiti Subdivision" (*ibid.*, *Geol. Survey Branch Bull.*, 41 (N.S.), 1946, 89 pp.).

Some general papers on Africa, West Indies, etc., are: G. M. Stockley, "The Geology of Basutoland" (*Geol. Mag.*, LXXVII, 1940, 444–60); P. E. Kent, "The Age and Tectonic Relationships

of East African Volcanic Rocks" (*ibid.*, LXXXI, 1944, 15–27). In regard to the latter see a discussion by W. Pulfrey (*ibid.*, 191–2); R. H. Palmer, "Outline of the Geology of Cuba" (*Journ. Geol.*, LIII, 1945, 1–34); D. W. Bishopp, "Some Problems of Geomorphology and Continental Relationships in British Guiana" (*ibid.*, LXXVII, 1940, 305–29).

The huge quarto memoir "L'Éodévonien de l'Ardenne et des Régions voisines," by E. Asselberghs (*Mém. Inst. Géol. Univ. Louvain*, XIV, 1946, 598 pp.), is a synthesis of numerous studies extending over a period of more than thirty years. The Eodevonian, it is concluded, is a natural stratigraphical unit which corresponds to a vast sedimentary cycle. Beginning with a transgression which reached its maximum in the Middle Siegenian, it was terminated by a very great recession.

The broad median zone of Iceland composed of younger rocks (Pliocene to Recent), and flanked on both east and west by great spreads of Early Tertiary basalts, has recently been interpreted by R. A. Sonder as a horst ("Zur magmatischen und allgemeinen Tektonik von Island," *Schweiz. Min. Petr. Mitt.*, XVIII, 1938, 429). This highly improbable suggestion, based as it is on inadequate and misinterpreted evidence, is easily controverted by L. Hawkes in a paper "Icelandic Tectonics—Graben or Horst" (*Geol. Mag.*, LXXVIII, 1941, 305–8), and the true interpretation of the structure as a graben rehabilitated. Dr. Hawkes also takes the opportunity of correcting other astonishing misstatements.

The "Hecla Hoek Rocks of New Friesland (Spitsbergen)" have been described by W. L. S. Fleming and J. M. Edmonds (*Geol. Mag.*, LXXVIII, 1941, 405–28). The most important new point is the confirmation of Blomstrand's early observation that not only is there a gradual decrease in metamorphism eastward from the gneissic belt to the typical Hecla Hoek rocks, but there is a similar decrease to the westward. The authors have examined a number of new areas in which, with the same general series of rocks (*i.e.* Hecla Hoek), there is a gradual increase in metamorphism westwards. The rocks have been isoclinally folded (Lower Murchison Bay formation), followed by igneous intrusion, and finally metamorphism of the whole assemblage.

W. B. Harland's "Geological Notes on the Stubendorff Mountains, West Spitsbergen" (*Proc. Roy. Soc. Edin.*, LXI, Pt. II, 1941, 119–29) show that this region consists of schists, gneisses and granulites belonging to the "Western Schists and Gneisses," which are now generally regarded as the equivalents of the Hecla Hoek formation. The metamorphism is believed by most workers,

including Harland, to be Caledonian. The tectonics of the area are extremely complicated, and observations recorded in this paper suggest recumbent folding and thrusting with nappe structure. Carboniferous rocks are recorded in this locality for the first time.

The stratigraphy and palæontology of the earliest Triassic has been studied by H. Frebold (*Norges Svalbard- og Ishavs-Undersökelser. Skr. om Svalbard og Ishavet*, No. 77, 1939, 58 pp.) at a number of localities along the west coast of West Spitsbergen. He makes faunistic comparisons with contemporaneous strata in East Greenland and the Ussuri district of northern Russia.

PEDOLOGY.

By G. V. Jacks, M.A., Imperial Bureau of Soil Science, Rothamsted Experimental Station, Harpenden.

Soil Classification.—The term "catena" introduced by G. Milne (*Soil Res.*, 1935, **4**, 183–98) for a complex of soil types genetically unrelated, or not necessarily related, but linked by conditions of topography and found in the same association wherever similar topographical conditions occur, has now passed into general usage, and the concept of the catena has proved of great value in soil and land classification, particularly in tropical regions. T. M. Bushnell (*Soil Sci. Soc. Amer. Proc.*, 1946, **10**, 335–40) has reviewed the various interpretations of the catena concept by different workers. He himself has made extensive use of it in the classification of Indiana soils (*Purdue Univ. Agric. Expt. Sta. Spec. Circ.*, 1, 1944, pp. 52). In general, soil series are accepted as the units of which catenas are composed, but Bushnell points out that some series in the American system of classification cover too wide a range of, say, drainage conditions to be considered as "units," and suggests that such series should themselves be regarded as catenas. In an earlier paper (*Soil Sci. Soc. Amer. Proc.*, 1943, **7**, 466–76) he pointed out that characteristics and types of soils form a continuous spectrum, and that breaking up this band into classes is quite an arbitrary procedure. He maintains that the formation of a catenary sequence is related to the water regime of the area where the catena occurs, and the water regime, in turn, may depend on slopes, water tables, porosity, water supply, etc.

Bushnell considers that all soils can be classified in relation to the water régime, in which case there would be no such thing as a non-catenary soil. He extends Milne's original idea of the catena as an essentially topographic sequence, and distinguishes *chrono-catenas* related to time, *byndels* related to parent material, *flor-catenas* related to vegetation, *climo-catenas* related to climate in

general, *hygro-catenas* related to the moisture component and *thermo-catenas* related to the temperature component of climate.

From a study of the catena relations of the soils of the Sudan, H. Greene (*Soil Sci. Soc. Amer. Proc.*, 1946, **10**, 392–5) concluded that tropical soils formed from acid and basic rocks tend to be alike when rainfall is high and drainage is good, but diverge under drier conditions and when drainage is impeded. The catena concept gives a clearer understanding of the relationships of tropical soils by emphasising that dissolved substances will move downhill, so that substances leached from a higher-lying member of a catena are deposited in the lower-lying members. This implies the inadequacy of the ABC system of profile-horizon description that recognises only a vertical movement of water, whereas the catena concept recognises the fact that water moves downhill.

The catena is clearly not a soil "type" and cannot find a place in any system of soil classification. It is a geographical unit which has proved its value and is, indeed, coming to be regarded as indispensable in soil mapping. J. Thorp and M. Baldwin (*Soil Sci. Soc. Amer. Proc.*, 1939, **3**, 260–8) state that "the catena cuts directly across the taxonomic classification. It is distinctly a geographic unit of classification and its members go to make up a typical composite landscape."

An overlap of the classification of soils and of geographical regions is a feature also of recent Russian work on soil classification. I. P. Gerasimov, A. A. Zavalishin and E. N. Ivanova (*Pedology*, 1939, No. 7, 10–43), in formulating a new scheme for a general soil classification for the U.S.S.R., state that "in so far as geographical conditions are combined in more or less uniform natural macro-complexes (geographical landscapes) and are distributed throughout a definite area, the genetic soil types are the main geographical elements of the soil cover; they are repeated regularly or remain constant throughout entire bioclimatic zones of the earth's surface."

According to this scheme the fundamental unit of soil classification is the genetic type, of which ten are distinguished, omitting soils of the tundra, mountain regions and the tropics and sub-tropics. These are divided into sub-types, developing in more or less similar geomorphological conditions and distinguished mainly by their vegetation, *e.g.* meadow and steppe solonets. Each of the types and sub-types can be further divided into five series related to the local climate or hydrothermal regime of the soil, *viz.* (1) the alluvial-plain series (river flats, subject to annual flooding), (2) the ground-water series (in which ground water is the dominant soil-forming factor), (3) the eluvial hydromorphic series (subject to

excessive leaching), (4) the eluvial series (containing the most characteristic climatic soils) and (5) the eluvial xeromorphic series (formed under relatively dry conditions). Soils of series (2) can be subdivided into three sub-series according to whether the ground water is strongly, moderately or weakly mineralised, and of series (4) into three sub-series according to whether the parent rock contains salts, carbonates or neither.

Not all the series are known for each soil type. The set of series within a type, however, presents a marked similarity to Milne's and Bushnell's concepts of the catena.

Series or "species" are the smallest taxonomic unit recognised in the scheme, but the authors point out that further subdivision can be made according to the quantity and quality of salts in saline soils, or to the humus content and thickness of chernozems, and so on, and varieties can be distinguished according to mechanical composition. Finally, varieties can be subdivided into cultural variants according to the degree to which they have been changed by cultivation.

Stress is laid in this paper and in a later paper by S. A. Zakharov (*Pedology*, 1943, No. 8, 26–35) on the inter-relationships of the separate genetic soil types. They are regarded not as isolated phenomena, but as stages in the evolution of a universal soil-forming process which may branch out in numerous directions, but of which an early stage is represented by saline soils and later stages by podzolised soils in temperate, and by lateritic soils in tropical, regions. Time is recognised as a soil-forming factor of equal significance with climate, geology, vegetation and topography. According to Gerasimov (*Pedology*, 1942, No. 7, 3–14) the new classification "asserts the essential unity of the geographical and genetic aspects of soil systematics."

A. A. Rode (*Pedology*, 1946, No. 7, 400–1) adds three additional soil-forming factors to the five listed above, namely, gravitation, water (surface and underground) and agriculture. He regards soil formation as a cyclic process subject to rhythmic fluctuation depending on the varying intensity of solar radiation. The most important cycles are the daily and yearly cycles, but there are others, *e.g.* the 11-year sunspot cycle. These cycles are never closed, and cause permanent changes in the soil. The net result of these changes is known as soil evolution. The soil is part of a wider complex—"biogeocoenose"—embracing the soil, the lower layers of the atmosphere, surface and ground water and living organisms.

A. R. Meshkov (*Pedology*, 1946, No. 4, 239–42) suggests that the

land surface of the earth should be divided into (1) groups of soil zones, (2) separate zones distinguished according to the dominant soil-forming process or soil type, (3) provinces distinguished according to conditions of climate, vegetation, geomorphology, etc., (4) districts distinguished geomorphologically, (5) regions distinguished according to the nature of the parent rock, and (6) micro-regions characterised by definite combinations of soil varieties.

In the first category three groups of zones are distinguished: (1) the holarctic group, (2) the pantropical group, and (3) the antarctic. The holarctic group covers the major part of the northern hemisphere, and most of the soil materials are of quaternary origin or underwent geological change in the quaternary period of glaciation, æolian action and submergence in the sea. The soils are extremely varied, and eight major zones are included in the group. The pantropical group includes the zones of lateritic and red and yellow tropical soils. These derive mainly from tertiary or earlier times and are much more mature than the holarctic soils. Eight zones are distinguished, lying within the tropics. The antarctic group, lying to the south of the tropic of Capricorn, is the smallest in area and also has the smallest variety of soils. Three zones are distinguished.

S. R. Crocker (*Counc. Sci. Indust. Res. Australia Bull.*, 1946, **193**, pp. 56) has described the inter-relationships through past climatic and geological history of apparently unrelated genetic soil types in South Australia. Many of the soils, including laterites, desert soils, leached siliceous sands and mallee soils (solonised brown soils), are "polygenetic" and have certain fossil characteristics related to past periods of their history. These, as well as the commonly occurring terra rossas, rendzinas and podzols are all closely linked with either the warm humid Pliocene, or with the Pleistocene glacial and interglacial periods, or with a Recent severe arid cycle. Crocker offers an explanation of the heavy accumulation of calcareous material and travertine horizons in many South Australian soils. He suggests that the calcium carbonate is derived largely from calcareous loessial material blown inland as a result of the winnowing of the coastal dunes or æolianite formed during exposure of large areas of the continental shelf with the swinging sea level of the Pleistocene. A diagram is given in which the genetic linkages between the main soil types are shown in relation to climatic changes during the Pleistocene and Recent periods.

L. J. H. Teakle, however, found no support for this theory from a study of the succession of soils from the coast inland in Western Australia (*J. Aust. Inst. Agric. Sci.*, 1946, **12**, 55–6). Here there

is a very close relationship between soil type and underlying rock, both in the red-brown and the solonised-brown soil zones. The substantial accumulation of $CaCO_3$ in the subsoil appears to be the result of simple pedogenic processes involving chiefly the parent material, leaching by rain, and the circulation of minerals by the vegetation. The latter sometimes has considerable significance. In one soil complex, consisting of a highly calcareous soil and a solonets, the only difference in pedogenic factors was a species difference in the *Eucalyptus* vegetation: on the calcareous soil the dominant species were *E. oleosa* and *E. conglobata*, whereas on the solonets they were *E. eremophila*, *E. dumosa.*, *E. flocktonia* and *E. gracilis*.

Soil Geochemistry.—V. M. Goldschmidt (*Soil Sci.*, 1945, **60**, 1–7) has shown how the determination of the atomic and ionic radii of a large number of elements entering into the structure of clay crystals has enabled a prediction of the occurrence of the elements in different minerals to be made. The entry of ions or atoms into the three-dimensional network of crystals is determined by their relative sizes, and the order of their entry by interatomic binding forces. Large-scale isomorphous substitution in minerals from magmas is in general limited to such pairs of ions whose radii agree within 10 to 15 per cent. of the larger radius of the pair. Thus iron (radius 0·83 Å.) and magnesium (0·78 Å.) freely replace each other in ionic crystals, but not magnesium and calcium (1·06 Å.). Manganese (0·91 Å.) can enter into isomorphous replacement of either calcium or magnesium. It is thus possible to classify the elements according to their atomic and ionic radii into a number of groups within which isomorphous replacement is possible, and thus predict the original magmatic minerals in which trace elements in particular are likely to occur.

Other principles, however, may be expected to govern the distribution of elements in sedimentary rocks and soils. Goldschmidt showed that the ionic potential (ionic charge/ionic radius) is a determining factor. Elements of low ionic potential tend to form cations in solution, those of intermediate ionic potential tend to remain as oxides or hydroxides (*e.g.* Fe, Al), while those of very high ionic potential form the central element (Si) of oxyacid anions.

The Rôle of Micro-organisms in Soil-structure Formation.—Much attention has recently been paid to the nature of the substances causing the aggregation of soil and of the agents producing those substances. T. M. McCalla (*Soil Sci.*, 1945, **59**, 287–97) has shown that most of the main groups of organic substances occurring in soil, including fats, waxes, lignins, oils, proteins,

resins, certain decomposition products of bacteria and fungal filaments, can have a direct stabilising effect on soil aggregates, but carbohydrates do not, though they may increase microbial numbers and thereby the quantity of microbial tissue and decomposition products which are effective in soil stabilisation. Data obtained by H. E. Myers and T. M. McCalla (*Soil Sci.*, 1941, **51**, 189–200) indicated that the relationship between bacterial numbers and aggregation was very complex, and that bacteria were associated with aggregation only through the accumulation of metabolic products which act as cementing agents. T. C. Peele (*J. Amer. Soc. Agron.*, 1940, **32**, 204–12) found that addition of sucrose promoted the formation of large, water-stable aggregates, and attributed the effect to the stimulated production of microbial mucus. J. P. Martin and S. A. Waksman (*Soil Sci.*, 1940, **50**, 29–47) found that the binding effect on soil particles produced by pure and mixed cultures of micro-organisms was caused partly by the mechanical binding of fungal mycelia and partly by synthesised organic compounds. When sugar was used as the source of energy for the micro-organisms a greater binding effect was obtained than when cellulose was used, and in general the more readily decomposable the organic substrate the greater the aggregating effect. J. P. Martin (*Soil Sci.*, 1945, **59**, 163–74) inoculated sterilized soils with pure cultures of various organisms, and made aggregate analyses after three weeks' incubation at 25° C. A species of *Bacillus subtilis* produced the greatest aggregation (67 per cent.), followed by the fungus *Cladosporium* (66 per cent.). These two organisms were then grown in liquid culture to determine whether the aggregating substances could be produced outside the soil. The liquid culture of *B. subtilis*, when added to soil, brought about even greater aggregation than the organism itself, but the culture of *Cladosporium* had a much smaller effect. Treatment of soil with liquid culture of *B. subtilis* freed from cells, and with cells alone, showed that the former was much the more effective aggregating agent—*i.e.* the most active agent was a substance synthesised by the cells. It was concluded that about half of the aggregating influence of *Cladosporium* was due to the binding effect of the fungus mycelia on the soil particles. The use of different sources of nitrogen and carbohydrate for growing the bacillus had little effect on the production of aggregating substance, except that sucrose was more efficient than other sugars.

From the centrifuged and dialysed culture media a crude substance was obtained, containing 42 per cent. carbon and reducing Fehling's solution after hydrolysis. This substance appeared to

be a hemicellulose-like substance which was attacked to a limited extent by fungi, and was readily destroyed by bacteria and actinomycetes.

In analogous experiments with calcareous soils, however, D. S. Hubbell and J. E. Chapman (*Soil Sci.*, 1946, **62**, 271–81) found that aggregation never occurred except in the presence of living microbes. This confutes Martin's conclusion that the main effect of micro-organisms on aggregation is attributable to cell secretions. Tests were made with bacteria, actinomycetes, fungi and the roots of Sudan grass. Each group of micro-organisms was capable of forming aggregates, but aggregation was less in cultures of bacteria than of fungi or actinomycetes. Sudan-grass roots did not produce any soil structure in sterile cultures. Two kinds of water-stable structures were present in the soil: microbial structures comprising soil particles held together by micro-organisms and root structures, and compound aggregates comprising microbial aggregates and entrapped soil particles held together by roots. The first are referred to as aggregates and the second as root structures. Stable soil structure in the field samples was always associated with a good growth of roots and micro-organisms. Roots contributed to structure formation only after this had been initiated by microbes, which were found in every root structure examined. Only after aggregates had been formed by microbes could roots synthesise larger structures by binding them together.

In his latest paper (*Soil Sci.*, 1946, **61**, 157–66) Martin identified the polysaccharides synthesised by and prepared from pure cultures of certain bacteria as fructosan and dextran containing a trace to 14 per cent. of uronic acids. These polysaccharides were better aggregating substances than casein or alkali-lignin, with which they were compared. The most efficient aggregating agent was a dextran synthesised by an unidentified soil bacterium. The dextran contained by far the highest content of nitrogen (1·52 per cent.) and of uronic acids (14·4 per cent.) of any of the preparations used. The polysaccharides were fairly resistant to microbial decomposition, possibly owing to their uronic-acid content, though there were always some organisms capable of utilising them.

BOTANY. By Professor W. H. Pearsall, D.Sc., F.R.S., University College, London.

Morphology.—In his Presidential Address to the American Society of Naturalists (*Amer. Nat.*, **80**, 497, 1946), E. W. Sinnott has recently discussed the bases of morphogenesis, and has developed the point of view that this branch of study, particularly the developmental

changes involved in the sequence, fertilised egg to mature organism, includes problems which go outside our knowledge in almost every discipline involving protoplasm and its activities. The mechanisms which control the process of development, and which bring it back to its normal path when accident or experimental change have diverted it, are little understood, even though many of the best brains in biology have attacked these problems. Dr. Sinnott contrasts, however, two highly divergent points of view. The most popular outlook today he regards as essentially that of the biochemist, the discovery of chemical substances which have far-reaching effects on development like the pituitary hormone in affecting body size and the male sex hormone in affecting body form. In botany, the hypothetical rhizocalines and caulocalines of Went are the complete expression of this creed and, incidentally, a return to the ideas of Sachs half a century ago. But this biochemical outlook results in each problem of development being followed by the search for or assumption of a *substance* which can produce the effect required. Valuable as are the results which have been achieved by this mode of attack, it fails to satisfy some of the most pressing needs of the biologist. The basic biological problem in growth, as in almost every other set of reactions, is one of *organisation*. The chemical reactions going on in the tissues are knit together in such an orderly fashion that an integrated whole is the result, an *organism* in short which maintains its unity in development and response as well as in maturity. Even if we regard this system as a series of chemical equilibria and steady states, the system retains its individuality, and it is quite reasonable to suppose that different organisms may react in different manners to the same substance. From this point of view, the chemical substance may be an *evocator*, acting on the developing system in such a way as to produce a morphological result. It by no means follows that a given substance will evoke the same results. Thus a nickel will activate a dial telephone or open a subway turnstile. A cent will not do these things but it will obtain a ticket with one's weight from a weighing machine. A quarter will do none of these things, but has a unique capacity for activating a gas meter. Thus while there is a certain specificity in these coins, an explanation of what they accomplish will only result from a study of the complex mechanisms they activate. Does not this give us a sound analogy with our morphological problems? No analysis, however complete, of substances known to have morphogenetic effects will explain their effects. Only a knowledge of the organised systems on which they act will solve the problems involved.

Post-glacial History.—The great interest which is being taken in the post-glacial period by botanists has been recently reflected in a number of papers. Pollen analysis continues to offer a satisfactory basis for much of the work done, but there are many and welcome signs that a considerable widening of the field of attack is taking place. Much the most extensive piece of work comes from North America, where H. P. Hanson has investigated the post-glacial forest succession, in relation to climate and chronology in the Pacific North-west (*Trans. Amer. Phil. Soc.*, N.S., **37**, Part 1, 1–180, 1947). The work was carried out over a wide area from Puget Sound to northern Idaho and it covers regions of widely differing climatic character and vegetation. Various types of peat and lake sediments were examined and their rates of deposition estimated. Pollen estimates were made and there is also an account of the local forest trees and their ecological preferences. Very many of the sedimentary profiles can be calibrated because of the presence of a layer of volcanic ash or detritus at a depth estimated to represent an age of about 6000 years. From the nature of the vegetation this is considered to have occurred in the middle of a period of maximum warmth and dryness. There is very generally a maximum of grass pollen just before it and in the southern localities a marked abundance of Chenopods—believed to be associated with the presence of arid conditions and of numerous alkali areas.

The sequence of tree pollens varies greatly in different places—but the changes are interpreted as representing variations in temperature and humidity. In the north, the recent phase of western hemlock, *Tsuga heterophylla*, was preceded by a long persistent forest phase of Douglas fir. In the southern areas, on the other hand, the more recent invasion of western white pine, *P. monticola*, had been preceded by the lodgepole pine, *P. contorta.*

The various changes appear to have culminated at similar periods, so that a general chronology is suggested of a preliminary colonising phase after glaciation, say 18,000–15,000 years ago, followed by a cool moist period until about 8000 years ago. This was followed by the maximum of warmth and dryness and finally by the inauguration of a cooler and moister epoch some 4000 years ago. The dates are obviously centred around the volcanic period already mentioned and the chronology resembles that used in western Europe, although the lengths of the corresponding periods are somewhat greater. A full discussion and comparison with eastern American and European ideas is given.

Of European papers, three English ones are of interest. One of them, by V. M. Conway (*J. Ecol.*, **34**, 149, 1947), deals with the

pollen analysis and stratigraphy of the Ringinglow bog, near Sheffield, a mass of deep peat of the raised bog type among an area of extensive cotton grass bogs. It gives us for the first time a highly detailed account of deep peat from the southern Pennines as investigated by modern methods. The peat is essentially *Sphagnum* peat, with a lower zone of more mixed character, including heather and cotton-grass and a thin upper layer of blackish modern peat with only cotton-grass remains. The area was originally perhaps forest, clad with much pine, later developing into extensive marginal alder and birch scrub. This then finally became a wet heath and sphagnum bog some time after the onset of the mixed oak-alder phase in forest history. Of great interest is the period in which the upper *Sphagnum* peat started to develop. This was preceded by evidence of considerable increases in bog humidity, particularly by the prevalence of *Menyanthes* remains, for this is a species which grows in bog pools. The development of almost pure Sphagnum peat followed this phase.

Later still there is evidence in the decrease of the tree pollen of wholesale destruction of forests in the districts—assumed to be since approximately the twelfth century. Much use is made in this paper of suggestions recently put forward by H. Godwin (*Proc. Prehistoric Soc.*, 1946, Paper No. 1) in reviewing the relations between bog stratigraphy, climatic changes and archæology. Dr. Godwin deals particularly with the stratigraphy of raised bogs, and in particular with the marked transition in peat character that usually takes place in the upper layers—the so-called "Grenz-horizon," a boundary layer that has in general been correlated with a period of approximately Bronze Age–Iron Age. The Grenz-horizon is due to a period of slow or negligible bog growth being followed by particularly active development. Granlund's work in particular has led to the recognition of five of these layers at various times between 2300 B.C. and A.D. 1200, and Godwin has given reason for believing that the third, about 600 B.C., is often strongly represented in England—though it is recognised that this may have been preceded and followed by other agencies and symptoms of change.

In the work on the Pennine bog, Dr. Conway has made use of this suggestion—equating the period of *Menyanthes* remains with the wet period of Granlunds phase IV *ca.* 1200 B.C. and the renewed rapid bog with Granlunds phase III *ca.* 600 B.C.

Another British paper dealing with certain aspects of post-glacial vegetation is by W. H. Pearsall and W. Pennington (*J. Ecol.*, **34**, 137, 1947). It records certain features, including pollen records and the organic content of the mud layers from sediments recovered

from the bottom of Windermere, and interprets them in the light of English Lake District history, which appears to have been of an especially simple type. As judged by the records from the sediments, a long period seems to have elapsed in which there was little or no change in the forest conditions, assumed to be alder woods in the valley bottoms and oak woods on the slopes. At a time, which coincides with the arrival of early man (Neolithic), however, changes occur both in pollen composition and in the percentage of organic matter in the muds. The latter first rise and then fall to an extremely low level, and it is suggested that these changes represent the period of human exploitation. At first, it is suggested, forest destruction was associated with the oxidation of organic matter, with soil leaching and with increased plankton growth and organic deposition in the lake. Later, the leached soils and probably soil erosion resulted in lower plankton growth and more inorganic silting in the lake. This latter stage corresponds in point of time with the removal of the valley alder swamps by Norse settlers and, later, with the economic exploitation of the district, which, by sheep-raising and iron smelting, resulted in almost complete deforestation. Each of the two main periods of change is marked in the lake muds by suggestive increases in the proportion of grass and sedge pollen.

The English papers mentioned are rapidly approaching the outlook more fully developed by R. F. Griggs (*Ecology*, **27**, 275, 1946), in which he emphasises the point of view that in order properly to interpret post-glacial history we need to know not only what were the vegetation trends in the past but also what are the present trends. In this paper he contributes particularly to the latter aspect of the problem, by attempting an interpretation of his work on North American timber-lines. Three areas are considered. In the vicinity of Kodial, Alaska, there is clear evidence that the coniferous forests are and have been spreading northwards for some 300 years at least. In the northern Rockies, however, the timber-line at higher altitudes is stable and appears to have been so for some 1500–2000 years. In New England, however, on Mount Washington, there is equally clear evidence of a recession of the tree limit, which has definitely become lower in the last fifty years, a change which seems to have been going on for a still longer period, probably some hundreds of years. The author points out that the trees concerned, mainly spruce and balsam, are also those which are concerned in the eastern Canadian forests described by Marie-Victorin, north of the Anticosti coast, where the spruce forests are considered to be dying off and doomed. He sees in this evidence a general tendency

for the timber-line to recede in eastern North America, pointing out that there is evidence from Greenland which suggests that a similar condition has long obtained there, for it is known that the early Norse colonies were unable to persist there after the twelfth century owing to climatic deterioration, that on many areas cleared of birches trees have been unable to re-establish themselves, and that many common and widespread Greenland plants are now unable to ripen seed. Indeed, Iversen, from pollen analyses, has concluded that the Greenland climate has been deteriorating for the last 2500 years. As the result of this survey, the author enquires whether it is certain that the destruction of forests in eastern North America by the wood-pulp industry will always be followed by the re-development of forests on the cleared area—a pertinent question which might also have been applied to some of the original woodlands in northern Britain.

PLANT PHYSIOLOGY. By Professor Walter Stiles, Sc.D., F.R.S., The University, Birmingham.

Trace Elements.—The status of manganese in the soil in relation to the incidence of manganese deficiency in plants, particularly in peas, has been discussed by Miss S. G. Heintze ("Manganese Deficiency in Peas and other Crops in relation to the Availability of Soil Manganese," *Journ. Agric. Sci.*, **36**, 227–38, 1946). The following manganese fractions in soils were determined: (1) total manganese, (2) exchangeable manganese, that is, the manganese obtained in solution when the soil is shaken with N calcium nitrate, (3) readily reducible manganese obtained by extracting the soil with N calcium nitrate containing 0·2 per cent. hydroquinone and (4) the manganese extracted with a warm solution of 0·2 M sodium hexametaphosphate. As regards exchangeable manganese it was found that this falls steadily with increase in *p*H such as is brought about by liming. This was shown very clearly by an experiment in which samples of a clay loam were incubated for a week with various quantities of added lime. The control with a *p*H of 4·5 contained 10·2 mg. per cent. of exchangeable manganese, whereas the samples with 1, 3, 8 and 12 tons of added lime per acre had *p*H values of 5·5, 6·3, 7·5 and 7·9 respectively with corresponding exchangeable manganese contents of 10·0, 8·4, 5·0 and 2·0 mg. per cent. This fall in the value of exchangeable manganese is attributed to oxidation of the manganous ion. Conversely, acidification generally increases the content of exchangeable manganese. For this reason addition of sulphur, which should increase soil acidity,

has been employed in order to increase the exchangeable manganese content, but the effect of such addition may be slow and slight. In general, it may be said that a considerable increase in soluble manganese only takes place when the soil reaction is brought well on to the acid side. Altering the oxidation-reduction state of the soil by waterlogging can increase the exchangeable manganese content, and application of reducing agents, such as sodium sulphite and hydroquinone, had previously been found to increase the soluble manganese content in pot cultures. In the field, however, where soil conditions were probably drier, Miss Heintze found no such effect. Direct addition of manganese sulphate may have little effect since the manganese may be rapidly oxidised, although with a reclaimed heath soil from Shropshire complete control of manganese deficiency in peas was achieved in this way although the amount of exchangeable manganese remained low. It would thus seem that the amount of exchangeable manganese is not always a good index of manganese availability. However, Miss Heintze found that neither of the other two fractions mentioned above proved any better for characterising manganese-deficient soils.

It has been known for some time that symptoms of manganese deficiency are liable to develop in plants growing on certain soils rich in humus, which suggests that the nitrogen status of the soil may be a factor in determining manganese deficiency. This view is supported by the finding that soils containing more inorganic nitrogen produced crops suffering from manganese deficiency whereas otherwise similar soils with less inorganic nitrogen did not. Also in field trials with a reclaimed neutral heath soil from Shropshire it was found that addition of ammonium sulphate increased the severity of the symptoms of manganese deficiency in oats, sugar beet and peas.

A further interesting finding of Miss Heintze was that peas grown in pot culture required an adequate supply of manganese throughout the whole period of seed formation. Manganese accumulated in the plant earlier was apparently not utilisable for seed production.

H. G. Dion and P. J. G. Mann ("Three-valent Manganese in Soils," *Journ. Agric. Sci.*, **36**, 239–45, 1946) find that the product of oxidation of divalent manganese in soils is three-valent manganese and they think this exists in the soil as hydrated manganic oxide $Mn_2O_3 \cdot xH_2O$. This substance dismutates into MnO_2 and divalent manganese under weakly acid conditions. The amount of divalent manganese in the soil at any time will be the result of an equilibrium

between the relative rates of oxidising processes on the one hand, and reducing and dismutating processes on the other.

A relation between iron and manganese in the metabolism of the plant has been suspected for a long time. E. S. Twyman ("The Iron-manganese Balance and its Effect on the Growth and Development of Plants," *New Phyt.*, **45**, 18–24, 1946) has produced a useful summary of the literature of this subject. It is interesting to note that nearly one hundred years ago, in 1848, Count Salm-Horstmar described the now well-known symptoms of manganese deficiency ("grey speck") in oats as occurring in cultures supplied with iron but without manganese, whereas when both iron and manganese were supplied the plants were free from these symptoms. During the present century a number of observations have been made indicating a close connection between iron and manganese in the plant. Recently the question has been dealt with by T. Wallace and E. J. Hewitt in a paper dealing with iron deficiency in crop plants ("Studies in Iron Deficiency of Crops. I. Problems of Iron Deficiency and the Interrelationships of Mineral Elements in Iron Nutrition," *Journ. Pomology and Hort. Sci.*, **22**, 153–61, 1946). Their record of the occurrence of both iron deficiency and manganese deficiency in the same plant, as in apples, plums, peaches and raspberries, is important in view of the theory of Somers and Shive that manganese deficiency symptoms result from a too high iron : manganese ratio in the plant and iron deficiency from a too high manganese : iron ratio, so that, in effect, iron deficiency is the same thing as manganese excess, and manganese deficiency the same thing as iron excess. Wallace and Hewitt, moreover, also point out that although manganese excess may produce chlorosis, it does not do so in all plants, while when it does other symptoms may accompany the chlorosis and its visual pattern may differ from that of iron chlorosis. This has been shown to be so with beans by T. Wallace, E. J. Hewitt and D. J. D. Nicholas ("The Resolution of Factors injurious to Plants on Acid Soils," *Nature*, **156**, 778, 1945).

R. MacVicar and B. E. Struckmeyer ("The Relation of Photoperiod to the Boron Requirement of Plants," *Bot. Gaz.*, **107**, 454–61, 1946) have examined the effect of boron shortage on the growth of soya bean plants exposed to different daily periods of illumination, namely 9 hours and 17–18 hours. In an experiment carried out in the spring, about 3 weeks after seedlings in pot culture were transferred to these respective conditions no visible differences could be detected in the short-day plants between those supplied with boron and those without added boron. With the long-day plants, how-

ever, reduced growth of the boron-deficient plants was already visible and a month after transference to the long photoperiod condition these plants exhibited the typical symptoms of boron deficiency, involving brittleness of the leaves, necrosis of meristematic tissue and reduction of secondary-root formation. After a further 25 days the symptoms of boron deficiency in these plants was very severe, whereas the corresponding plants exposed to normal daylight showed only moderately severe symptoms, and the short-day plants were essentially normal. Confirmatory results were obtained in a similar experiment carried out in the autumn. These observations confirm the earlier experience of Miss Warington, who found that shortened days retarded the appearance of symptoms of boron deficiency in broad beans and other plants.

The necessity of boron for the tobacco plant was demonstrated by T. R. Swanback twenty years ago. The same worker has now shown ("Boron in Tobacco Fertilization," *Soil Sci.*, **62**, 137–49, 1946) by means of field experiments and chemical analyses of soil and plant material, the importance of a proper balance in the soil between boron and other mineral nutrients, notably potassium and calcium, and it is suggested that the ratio $\frac{K \times B}{Ca}$ where K, B and Ca represent the proportions of these three elements in the plant, might be important in relation to crop yield.

R. MacVicar, W. E. Tottingham and G. H. Rieman ("Boron Supply and Boron Content of Potatoes," *Soil Sci.*, **62**, 337–40, 1946) have attempted to correlate the boron content of potato leaves and tubers with the available boron in the soil. To this end the soluble boron in a number of soils was determined together with the boron content of the leaves and tubers of potato plants growing on the respective soils. It appeared that variations in the boron content of the tissues could only be correlated with variations in the soluble boron content of the soil in soils of similar texture. With soils of different texture no such correlation was found. Thus plants growing on a peat with a soluble boron content about four times that of a sandy loam actually contained less boron than plants growing on the latter soil. As regards the actual content of boron in the plant it was found that the leaves examined contained normally from 22·0 to 49·9 p.p.m. (parts per million) and the mature tubers 6·4 to 14·3 p.p.m., based on dry weight. In experiments in which borax was added to the soil in quantities varying from 25 lb. to 150 lb. per acre, the amounts of boron in the leaves and tubers were much greater, rising with the highest

dressing of borax to 450 p.p.m. in the leaves and 121 p.p.m. in the tubers, although with this high boron content the crop yield was considerably reduced. It is concluded that when the quantity of boron in the leaf exceeds 300 p.p.m. this element is definitely toxic.

Boron deficiency in apples results in development in the fruit of internal cork, a condition which can be prevented by application of borax or boric acid to the soil. It thus becomes of interest to determine any effect of boron on the fruit during subsequent storage. This question has been the subject of investigation by M. H. Haller and L. P. Batjer ("Storage Quality of Apples in Relation to Soil Applications of Boron," *Journ. Agric. Res.*, **73**, 243–53, 1946). They found that increasing the boron content of the soil by a dressing of borax brought about a considerable increase in the boron content of the fruit, values 40 p.p.m. or higher being observed as compared with normal values in the region of 12 to 20 p.p.m. Sometimes the application of borax to the soil induced earlier maturity as indicated by earlier dropping of the fruit and the colour change from green to yellow and red. On the other hand, the increased boron content was not associated with any appreciable effect on acidity, solute concentration or dessert quality. In Jonathan apples excessive boron greatly increased the tendency to internal breakdown during storage whereas in some other varieties such as Declicous storage scald was definitely reduced in fruit with a high boron content.

A study, largely microchemical, of the effect of zinc deficiency on tomato plants has been made by H. S. Reed ("Effects of Zinc Deficiency on Phosphate Metabolism of the Tomato Plant," *Amer. Journ. Bot.*, **33**, 778–84, 1946). The distribution of phosphates, oxidases and dehydrogenases was examined by means of microchemical tests applied to sections of tissue, while information about the sugar and starch in the leaves was obtained by chemical analysis. The general results of the investigation showed that plants suffering from zinc deficiency were stunted and pale green, there being inhibition of the development of meristematic tissue in the stem and hypertrophy of the mesophyll cells of the leaf. The stem contained more inorganic phosphate and oxidase in the phloem and extra-stelar region than did those of normal plants, but less dehydrogenase. It is concluded that the greater quantity of inorganic phosphate results from an increased amount of phosphatase in the affected plants. This disturbance of the phosphate metabolism in zinc-deficient plants results in disturbance of cellular activities as indicated by the abnormal condition of the meristematic and parenchymatous tissue. The leaves of zinc-deficient plants contained a higher percentage of reducing sugars but less

sucrose and starch than normal plants, which suggests that an enzyme system involved in carbohydrate metabolism, as for example zymohexase which is said to contain both copper and zinc, is put out of action in plants deficient in zinc.

Shortage of copper is known to produce on certain continental soils a pathological condition known as reclamation disease. An account of this, more especially as it affects the Netherlands, has been produced in book form by W. J. Melchers and H. J. Gerritsen (*Koper als onmisbaar element voor plant en dier*, Wageningen, 1944). The work is illustrated with a number of photographs, some in colour, which show the symptoms of copper deficiency in a number of species including oats, barley, canary seed, garden peas, potato, garden beet and sugar beet, meadow soft grass (*Holcus lanatus*) sheep's fescue (*Festuca ovina*) and marsh bent grass (*Agrostis alba*).

As with manganese, it appears that deficiency of copper may not always be due to an absolute shortage of the element in the soil, but that other factors may influence its availability to the plant.

The influence of copper deficiency on the metabolism of the tung tree (*Aleurites fordii*) is the subject of a paper by S. G. Gilbert, H. M. Sell and M. Drosdoff ("The Effect of Copper Deficiency on the Nitrogen Metabolism and Oil Synthesis of the Tung Tree," *Plant Physiol.*, **21**, 290–303, 1946). Disorders of this tree due to manganese and zinc deficiencies had already been known for some time. More recently a necrosis of the leaves was observed which appeared to be the result of copper deficiency; at any rate, the disorder was controlled by application of copper sulphate to the soil or by spraying the foliage with a solution of this salt. Gilbert, Sell and Drosdoff determined the carbohydrates, nitrogen fractions and copper in normal leaves and in leaves in which the pathological symptoms were just beginning to appear. The affected leaves contained less copper than normal ones, but also they contained less reducing sugar and very much less starch than normal leaves; the percentage of non-reducing sugar was much the same in affected and healthy leaves. The total nitrogen content of affected leaves was considerably higher than that of normal leaves, the high value being largely due to the water-insoluble nitrogen fraction. The conclusion drawn is that in copper-deficient plants abnormally large quantities of complex nitrogen compounds are formed at the expense of carbohydrate. In copper-deficient plants not only are the leaves affected but the seed is abnormally small and fat production is low.

The effect of copper deficiency on plant metabolism has also

been examined by J. G. Wood and H. B. S. Womersley ("Development and Metabolism of Copper-deficient Oat Plants," *Australian Journ. Expt. Biol. and Med. Sci.*, **24**, 79–94, 1946). The oat plant is particularly susceptible to copper deficiency, the symptoms being the absence of pigment in the leaves and their failure to unroll, failure of grain formation and excessive tillering. Oat plants were grown in pot culture under various conditions of copper and nitrogen supply, and copper, protein nitrogen, crude fibre and ascorbic acid determined in the plants after harvesting. All nitrogen-deficient plants, whether receiving additional copper or not, developed the symptoms of copper deficiency, but this was ascribed to poor root development. In the plants supplied with nitrogen but not with copper the percentage of protein in stems, leaves and roots was higher at late harvesting than in plants supplied with both nitrogen and copper. The copper-deficient plants behaved, in fact, like plants in which the inflorescence had been removed and in which vegetative growth continued; the protein hydrolysis which occurs in the vegetative organs of normal plants during maturation of the grain was very much reduced in the copper-deficient plants. In the latter it would thus appear that insufficient copper reached the flower to produce some essential copper complex. The amounts of copper found in the various parts supported this view, the total amounts in the inflorescence and grain of the copper-starved plants being very much less than the corresponding amounts in normal plants. Dead leaves were found to have a high percentage of copper, suggesting that the copper in leaves is relatively immobile and that the copper required for grain formation must come from the roots so that a continuous supply from the external medium is required throughout the life of the plant.

Miss K. Warington ("Molybdenum as a Factor in the Nutrition of Lettuce," *Ann. App. Biol.*, **33**, 249–54, 1946) has made a study of the effect of molybdenum on lettuce plants grown in water culture. Usually the molybdenum, as sodium molybdate, was supplied in a concentration of 0·1 p.p.m. In general, the plants supplied with added molybdenum produced more dry matter than the controls without added molybdenum and in a number of experiments the latter exhibited definite symptoms of what would appear to be molybdenum deficiency. Such plants were small, pale, and with a loose open habit, and as they approached maturity some of the medium-aged leaves developed patches of grey-blue crinkled tissue which later coalesced, turned yellow and papery, and finally withered, Although in some experiments plants without added molybdenum appeared quite healthy, Miss Warington concludes that molybdenum

plays an important part in maintaining a healthy condition in the lettuce plant.

The necessity of molybdenum for a number of Leguminosæ has been indicated in work by A. J. Anderson ("Molybdenum in Relation to Pasture Improvement in South Australia," *Journ. Council Sci. Ind. Res.*, **19**, 1–15, 1946). Field trials with certain soils showed that addition of molybdenum as molybdenum trioxide, sodium molybdate or ammonium molybdate, improved the growth and colour of a number of species of clover including *Trifolium subterraneum*, *T. glomeratum*, *T. procumbens* and *T. angustifolium*. When grown in pot cultures addition of molybdenum to the soil was found to increase the growth of both *T. subterraneum* and *Medicago sativa*.

K. C. Beeson, L. Gray and M. B. Adams ("The Absorption of Mineral Elements by Forage Plants: I. The Phosphorus, Cobalt, Manganese and Copper Content of some Common Grasses," *Journ. Amer. Soc. Agron.*, **39**, 356–62, 1947) have obtained information about the relative trace element contents of grasses belonging to fifteen species all grown on the same soil, a fine sandy loam. With reference to each element they arranged the grasses into three groups, namely, grasses with high, medium and low content of the particular element. The high manganese group contained from 815 p.p.m. (red top) to 261 p.p.m. (brome grass) of that element, the medium group from 195 p.p.m. (carpet grass) to 135 p.p.m. (Kentucky blue grass) and the low group from 107 p.p.m. (quack grass) to 96 p.p.m. (para grass). With copper the contents varied from 21 p.p.m. (Kentucky blue grass) to 12 p.p.m. (red top) in the high group, from 10·5 p.p.m. (Johnson grass) to 7·2 p.p.m. (Vasey grass) in the medium group, and from 6·8 p.p.m. (quack grass) to 4·5 p.p.m. (para grass) in the low group. The high cobalt group (Kentucky blue grass and carpet grass) contained about 0·13 p.p.m. of that element, the medium group, which included brome grass and timothy, about 0·08 to 0·09 p.p.m., while the low group contained from 0·05 to 0·07 p.p.m. of cobalt. The range of cobalt content was thus much narrower than that of either copper or manganese. No doubt considerably greater variations than those recorded would be found with plants grown on different soils, but work on these lines should prove of economic importance in regard to the nutrition of grazing animals.

ENTOMOLOGY. By A. D. Lees, M.A., Ph.D., Agricultural Research Council, Unit of Insect Physiology, Cambridge.

The Language of the Honey Bee.—A dish containing sugar water placed near a hive of bees may remain unattended for some time but, once it has been found by one bee, others from the same hive soon follow. Again, when a particular flower is discovered by a few bees, other foraging workers from the same hive may soon turn their attentions to this species to the virtual exclusion of other flowers. How is the knowledge of situation and of the flower species communicated ? These questions have recently been answered by K. v. Frisch in a remarkable series of observations (*Österreich. zool. Zeit.*, 1946, **1**, 1 ; *Experientia*, 1946, **2**, 1).

The language of the honey bee is one of scents and dances. The kind of flower visited is indicated by the scent adhering to the body of the homing bee ; but this becomes relatively faint if the bee is returning from far afield. A more permanent guide is provided by the nectar in the honey stomach, which retains the specific flower scent and is afterwards fed to other bees in the hive. The importance of such means of communication can be shown by feeding a bee on a droplet of sugar water which has absorbed the specific scent from a bloom of *Phlox*. If blooms of *Cyclamen* and *Phlox* are now placed near the hive the latter are visited exclusively, even though the nectar is accessible only to Lepidoptera. Bees can be made to acquire the scent of *Cyclamen* on their bodies and that of *Phlox* in their honey stomachs. In this way it is possible to show that the strength of the latter remains relatively undiminished even after a long flight.

By using a glass-fronted observation hive the dances of the returning bees could be watched. Bees dance only when food is abundant. Those informed by the scent then fly out and the number of visiting bees increases. Conversely, when there is little nectar about, dancing ceases and the number of foraging bees diminishes. In this way there is always a correct relation between the amount of nectar and the number of visiting bees.

The dances also have a significance that was previously unsuspected in conveying to other bees the distance of the feeding place from the hive. Bees collecting nectar at distances of less than 100 metres perform a " round dance " (*Rundtanz*), moving in a circle first in one direction and then in the other. Bees collecting at greater distances, on returning to the hive, perform a second " tail-wagging " dance (*Schwänzeltanz*), which consists of movements in a semicircle, alternatively to the left and right. The " tail-wagging " occurs between successive semicircular movements when

the bee is advancing in a straight line (the "straight run"). But the information imparted by the *Schwänzeltanz* is even more precise than this, for there is a very constant relationship between the rhythm of the dance (number of turns per unit of time) and the absolute distance from the hive.

Not only does the *Schwänzeltanz* convey the distance, but, more remarkable still, it indicates the direction of the feeding place by the orientation of the straight run. Running up the comb signifies that the feeding place is in the same direction as the sun; running to the left of the perpendicular by a certain angle means that food can be found in the same angle left of the sun; running downwards means that it is in the opposite direction to the sun, etc. Very few of the informed bees fly out in the wrong direction. If the comb is laid horizontally the *Schwänzeltanz* is still performed, but now the direction of the straight run indicates the situation of the food directly ("like a compass needle"). Dancing may indeed sometimes occur naturally on a horizontal surface, at the threshold to the hive, on a partly constructed comb, etc.

THE REPRODUCTIVE BEHAVIOUR AND ORIENTATION OF SOLITARY WASPS.—The nesting behaviour of the Sphecoid wasp *Ammophila adriaansei* has been described in two very interesting publications by G. P. Baerends (*Tijdschr. Ent.* 1941, **84**, 68; *Nederl. Akad. v. Wetensch.*, 1941, **44**, 1). The reproductive behaviour of the female wasp consists of coition, digging one-celled nests, capturing and paralysing caterpillars, which are then stored as larval food. Observations with marked wasps showed that one female usually tended two and sometimes three nests simultaneously and revealed a most interesting pattern of behaviour. During the first phase of activity the wasp digs nest A in flat sandy ground, closing the entrance with loosely fitting crumbs of soil. She then brings a caterpillar, reopens the nest, lays an egg and closes the entrance with greater care, thus completing this phase. She is then occupied for one day or more digging nest B and again completes the first phase. Next she visits nest A without a caterpillar, reopens it and disappears into the cell ("solitary visit"). If the larva has hatched she then brings 1–3 caterpillars ("provisioning visit") and again closes the nest. This second phase is then completed with nest B. During the third and final phase there is a further solitary visit to A followed by a provisioning visit with 3–7 caterpillars. The nest is then closed with particular care. Apart from the other activities of sleeping or foraging for herself the wasp is occupied with one nest only during each phase. Sometimes she digs a third nest before beginning the second phase in B.

By substituting for the real nest a plaster cell whose contents could be changed at will, the solitary visit was shown to be a visit of inspection. Thus it is the amount of food present during the inspection that determines the behaviour during the second and third phases. If, for example, the larva is replaced by an *Ammophila* egg and a caterpillar from another nest, the wasp does not immediately start provisioning after the first solitary visit as she would normally. Again, if the egg is replaced by a larva, fresh caterpillars are brought. Or if all caterpillars are removed before the occasional solitary visit half-way through the third phase, the wasp brings a great excess of caterpillars. Yet there is no response when the same changes in the cell contents are made before a provisioning visit. On the other hand, there is certainly mutual stimulation between the wasp and her larva and the passage from one phase to the next is probably regulated by the age of the larva she happens to find.

Of particular interest also are the means by which the fossorial wasps find and recognise their nests. Previous experiments with *Philanthus triangulum*, which captures and stores honey bees, showed that the visual recognition of landmarks was of paramount importance. By placing various objects round the nest entrance N. Tinbergen and W. Kruyt (*Z. vergl. Physiol.*, 1938, **25**, 292) were able to demonstrate that certain objects were preferred to others as training "beacons." Height was the most important characteristic, but other qualities, such as size, solidity and contrast, were also of significance. Training to a new situation takes place more readily after prolonged rain has obliterated the old landmarks. At first the wasp orients towards the complex of objects; later in the training experience particular objects in the assemblage may assume a special importance. How the wasps find their way back to the neighbourhood of the nest from far afield is less well understood, although N. Tinbergen and R. J. van der Linde (*Biol. Zbl.*, 1938, **58**, 425) have shown that, when wasps were captured and released at varying distances from the nest, the number which failed to return was much greater when they were transported in the opposite direction to their natural hunting ground, which in this case was a heath much frequented by bees. This suggested that only the territory over which they normally flew was well known to them.

Baerends investigated this problem in *Ammophila* by following the homeward route when the wasp and her caterpillar are released at some distance from the nest. If the larva is sufficiently small to be carried in flight the wasp makes a short, spiral orientation flight

before proceeding directly towards the nest. A heavy caterpillar, on the other hand, has to be dragged along the ground. When, as often happens, the wasp loses her way, she climbs a low tree or bush, after momentarily abandoning the larva, and appears to take stock of her surroundings. The correct route is again resumed after some conspicuous landmark, such as a particular tree, falls within the visual field. That orientation does in fact depend on the recognition of such landmarks was shown conclusively by constructing a row of dummy pine trees which were moved when the homing wasps had become accustomed to them.

Near the nest entrance the significant landmarks become progressively smaller, such objects as twigs, fir cones and tufts of grass being commonly used. Solid objects are again preferred to those without relief, although sand flecks are sometimes of significance. It is clear that with two or more nests under her care simultaneously the wasp must possess a remarkably retentive memory, particularly as she may be unable to visit her nests for days on end during bad weather.

THE CLASSIFICATION OF SIMPLE ORIENTING REACTIONS.—The innate responses of insects to elementary physical stimuli have been increasingly studied in recent years. The subject has been considerably developed by G. Fraenkel and D. L. Gunn in their book *The Orientation of Animals. Kineses, Taxes and Light Compass Reactions*, Oxford, 1940. Besides providing a summary of a large body of knowledge, much of it dealing with arthropod behaviour, these authors have been successful in clarifying and regrouping the various orientations so as to bring out the essential mechanisms concerned.

The importance of simple orienting responses in the life of an insect is well illustrated by the behaviour of the human body louse, *Pediculus humanus* (V. B. Wigglesworth, *Parasitology*, 1941, **33**, 67). When the louse is offered alternative stimuli in a choice chamber many of the reactions are undirected (kineses). The response may depend on the rate of movement (orthokinesis) as, for example, when the louse chooses rough in preference to smooth cloth by coming to rest more frequently on the former. Or, in responding to other diffuse stimuli, the rate of turning may increase when the louse encounters the unfavourable stimulus (klinokinesis); and if it fails to regain the favourable zone the track gradually becomes less convoluted as sensory adaptation takes place. This is the usual response to temperatures higher or lower than about 30° C., to high humidities or humidities to which the louse is unaccustomed, or to smells other than the preferred scents of man

and of louse excreta. In this response the louse is in no way attracted to the favourable stimulus. Instead it avoids a zone where an intrinsically repellent stimulus is present or where a favourable stimulus which has been recently experienced is absent.

Directed responses (klinotaxes) to diffuse stimuli come into play if the gradient is sufficiently steep. The louse then turns back immediately on entering the unfavourable zone. This orientation is probably brought about by successive comparisons of intensity as the antennæ (which bear humidity, smell and temperature receptors) are swung from side to side. Finally, in responding to darkness or lateral illumination simultaneous comparisons of light intensity by the eyes (tropotaxes) are of most importance. All these responses are of value in keeping the louse within its normal environment.

• THE STRUCTURE OF INSECT CUTICLE.—Since my last notes in SCIENCE PROGRESS, 1946, **34**, 609 on the subject of the insect cuticle further important contributions have been made towards the elucidation of its structure. Interest has centred particularly on the structure of the inner layers of the cuticle, on the nature of the hardening process, and on the structure of the "epicuticle" which, by the application of new methods, has been shown to be far more complex than was previously suspected.

The fine structure and chemistry of several insect cuticles has been re-examined by G. Fraenkel and K. M. Rudall (*Proc. Roy. Soc. B*, 1947, **134**, 111). Soft cuticles which yield the highest values for protein, contain chitin and protein in the approximate ratio of 55 : 45 corresponding, for equal chain lengths, to a ratio of one chitobiose unit to three amino-acid residues. X-ray examination showed that the protein moiety, unlike that of most vertebrate skeletal proteins, was in the form of extended β-protein chains. The fact that important features in the chitin diffraction pattern of intact cuticle depended on the stability of the protein suggested the presence of alternating monolayers of protein and chitin. The similar shape and spacing of the chains may permit the formation of stable, interpenetrating lattices.

Previous studies with the electron microscope by A. G. Richards and T. F. Anderson (*J. Morph.*, 1942, **71**, 135) had indicated that the endocuticle of the cockroach pronotum consisted of alternate layers of different density. This lamination, it was suggested, might be due to the presence of alternating layers of dense chitoprotein polymers and chitin relatively poor in protein. The endocuticle is penetrated by pore canals which are helical in shape and number about 200 to each epidermal cell. The electron micro-

graphs revealed the presence of at least two layers in the cockroach epicuticle. On the other hand, the endocuticle of mosquito larvæ was devoid of pore canals and the epicuticle appeared to consist of one uniform layer.

The structure and growth of the larval cuticle of *Sarcophaga* has been studied histologically by R. Dennell (*Proc. Roy. Soc. B*, 1946, **133**, 348). The soft endocuticle consists of two zones. The outer, which is deposited during early larval life, contains relatively large pore canals which stop short of the epicuticle. The inner zone is secreted later in larval life and is without pore canals. The latter, which are left isolated in the outer endocuticle, become filled with chitin. Two layers were again distinguished in the epicuticle, an inner protein layer and an outer resistant " lipoprotein " layer.

The nature and deposition of the outermost layers of the cuticle in *Rhodnius* have been examined in detail by V. B. Wigglesworth (*Proc. Roy. Soc. B*, 1947, **134**, 163). The " epicuticle " in this Reduviid is again composite and consists of four distinct layers, an inner " cuticulin layer " composed of polymerised lipoproteins tanned by quinones, a " polyphenol layer " rich in dihydroxyphenols, a " wax layer " responsible for the waterproofing of the cuticle, and an outer " cement layer " of unknown nature covering and protecting the wax. During the secretion of the new epicuticle the œnocytes, which become greatly lobulated, synthesise the lipoprotein, which is afterwards taken up by the epidermal cells and deposited as the cuticulin layer. Next, the polyphenol droplets appear at the tips of the pore canals which can be seen to penetrate the cuticulin layer. Later these droplets coalesce to form a continuous film. Wax is then secreted by the pore canals over the polyphenols, the continuity of this layer being finally established just before the shedding of the old cuticle. The cement is secreted by the dermal glands and is poured out over the surface of the wax within one hour of moulting. Wigglesworth emphasises the remarkable timing and co-ordination of these events, and the chemical range of the epidermal cells which are responsible for the secretion of all the cuticular layers with the exception of the cement covering.

Within the thick epicuticle of the louse *Eomenacanthus* J. E. Webb (*Parasitology*, 1947, **38**, 70) has detected four layers, of which the outer is a cement layer. The inner three layers, which are distinguished by their staining properties, may include a layer additional to those described in *Rhodnius*. All three are penetrated by the pore canals. Multi-layered epicuticles are also found in ticks (A. D. Lees, *J. Exp. Biol.*, 1947, **23**, 379). In the Argasidæ the epicuticle consists of four layers homologous with those in

Rhodnius. In the Ixodidæ, however, the cement covering is absent, leaving the wax layer freely exposed. A further difference between these two families concerns the nature of the waterproofing waxes. Without exception the Argasid waxes have higher transition temperatures and are more effective in preventing the transpiration of water. The Argasidæ live in very dry situations, whereas most species of Ixodidæ are found in much moister environments.

Further progress has recently been made in the identification of the phenolic substances responsible for the hardening process in insect cuticles, which has been shown to be due to a tanning of the cuticular proteins. M. G. M. Pryor, P. B. Russell and A. R. Todd (*Biochem. J.*, 1946, **40**, 627; Nature, 1947, **159**, 399) have isolated the tanning agents from several insects. The phenol extracted from cockroach oothecæ proved to be protocatechuic acid (3 : 4-dihydroxybenzoic acid). The reaction of this substance with the left (protein-secreting) colleterial gland is identical with the reaction when the contents of the left and right glands are mixed. Protocatechuic acid was also isolated from *Calliphora* puparia. *Tenebrio* adults, on the other hand, yielded a mixture of 3 : 4-dihydroxyphenylacetic and 3 : 4-dihydroxyphenyl-lactic acids. Now Fraenkel and Rudall have shown in the paper cited above that the substrate of the phenol is certainly tyrosine in the blood. Pryor, Russell and Todd therefore suggest that if, as appears probable, dihydroxyphenylalanine is the first product of the action of polyphenol oxidase on tryosine, the three phenolic acids detected by them represent a complete series of the stable degradation products of this substance. The mechanism of hardening is being studied further, but it probably involves the condensation of the *o*-dihydroxyacid with protein chains to form a stable cross-linked structure in which the nitrogen of the free amino-groups becomes attached directly to the aromatic nuclei.

A New Classification of Insect Pupæ.—In a paper of this title H. E. Hinton (*Proc. Zool. Soc. Lond.*, 1946, **116**, 282) has reconsidered the structural characters of pupæ in relation to the manner of emergence of the adult insect. The present classification recognises as principal types the exarate, obtect and coarctate pupæ of Linnæus. It is pointed out, however, that the last category is misleading as the puparium of the Cyclorrhapha is in the nature of a cocoon, the pupa it contains being typically exarate with free appendages. Hinton distinguished two primary classes of pupæ, the *pupa dectica*, possessing functional mandibles in the pupal stage, and the *pupa adectica* with non-functional mandibles. Decticous pupæ, which are all exarate, are found in the Megaloptera,

Neuroptera, Mecoptera, Trichoptera and primitive Lepidoptera. Among insects from these orders the mandibles are used for biting open the cocoon or pupal cell, the adult often walking some distance before casting the pupal skin. Adecticous pupæ, on the other hand, may be exarate or obtect. Evolution has in many cases tended to accentuate the obtect characteristics. The function of this increased "soldering" of the appendages is partly protective and partly to facilitate the escape of the pupa from the pupal cell. The escape of the adecticous pupa is often assisted by the presence of cocoon-cutters and arrangements of backwardly directed spines.

NOTES

Mutations Produced by Chemical Compounds

The discovery recently reported by Auerbach and Robson (*Proc. Roy. Soc. Edin.*, 1947, **62B**, 271, 284) of the production of mutations by chemical compounds is a most significant advance in genetics and in biology generally; it is also of particular interest to the biochemist. Since Muller's success in producing mutations by X-rays, many attempts have been made to induce them by chemical compounds. In the past positive results have been claimed, but the effects have always been small and of doubtful significance. Auerbach and Robson now report that mutations are produced in *Drosophila melanogaster* by treatment with mustard gas (dichlorodiethylsulphide, $S(CH_2CH_2Cl)_2$). The rate of mutation produced by sub-lethal doses of this compound may be of the same order as that produced by X-rays. Among 2750 sons of treated males there occurred 79 visible mutations, as compared with 6 among the same number of untreated males. As with X-rays, treatment with mustard gas produces, besides visible mutations, other evidence of chromosomic changes, such as sex-linked and dominant lethals, and chromosomic translocations and deletions.

Besides mustard gas, Auerbach and Robson have tested a number of other chemical compounds. Small, but probably real, effects have been observed with allyl *iso*thiocyanate. Much more striking effects have been produced by three compounds related to mustard gas and possessing the vesicant properties of the latter. These are: $CH_3N(CH_2CH_2Cl)_2$; $N(CH_2CH_2Cl)_3$; and $O(CH_2CH_2SCH_2CH_2Cl)_2$. In their mutagenic action these three compounds resemble mustard gas quantitatively and qualitatively. It is of interest that lewisite, $CHCl{:}CHAsCl_2$, a powerful, arsenic-containing vesicant, had no detectable mutagenic action.

Evidently we have in these mutagenic compounds chemical agents which enable us to modify the structure of the chromosome. A new field of research in genetics has thereby been opened up, and also a new approach has been made possible to the study of the chemistry of the gene and the enzyme systems which it controls. Furthermore, the proof that certain chemical substances definitely induce mutations makes it easier to explain the spontaneous mutation rate. This is higher than can be accounted for by thermal agitation cosmic rays and rays from radioactive materials. Auerbach and Robson discuss the possibility that natural mutations may,

in part, be the effect of the presence in the cell of metabolites with a mutagenic action. This hypothesis has many attractive features, and will no doubt be duly submitted to experimental tests.

An Exhibition of British Chemistry (**J. R. Ruck Keene**)

Petty nationalism is always undesirable ; but it was in no such spirit that the Chemical Exhibition, housed in the Science Museum through the courtesy of its Director, Dr. H. Shaw, was arranged. Indeed, there is every justification for placing before the overseas visitors to the Centenary Celebrations of the Chemical Society and the XIth International Congress of Pure and Applied Chemistry a comprehensive review of the scope and originality of the British contribution to chemistry. Moreover, the exhibition remains open until September 30th, so that a wider public can visit it.

The Exhibition has been arranged on behalf of the Chemical Society and the Congress by a Committee under the Chairmanship of Sir Robert Robertson, K.B.E., D.Sc., F.R.S., and is in two parts illustrating the history and applications of the science. The historical part has been arranged in sections each dealing with a broad division of chemistry. Each section has been in the care of a panel of experts responsible not only for the selection of the exhibits but also for the corresponding chapter of the handbook to the exhibition, *Chemical Progress*, printed by H.M. Stationery Office (price 1*s*. 6*d*.). The preparation has entailed considerable labour by a group of leaders in chemistry in Britain today and it constitutes a brief, authoritative, but comprehensive survey which may well become a valuable aid to future students and teachers of chemistry. The Chairmen of the panels are Dr. A. E. Alexander, Dr. G. M. Bennett, Professor J. D. Bernal, Professor H. V. A. Briscoe, Dr. E. M. Crowther, Professor C. W. Davies, Professor D. H. Hey, Professor C. N. Hinshelwood, Professor E. K. Rideal, Professor N. V. Sidgwick and Professor M. W. Travers. The reports of each panel were edited and correlated by Dr. F. Sherwood Taylor, Curator of the Museum of the History of Science, Oxford.

The modern section, which deals in a popular manner with "Chemistry in Everyday Life," was prepared by the Department of Scientific and Industrial Research, with the co-operation of the Agricultural Research Council, several Research Associations, and a number of industrial firms. The Central Office of Information have assisted in the design and layout of this part of the Exhibition, which relates theory to practice in such fields as Agriculture and Food, Health, Homes and Building, Fuels, Oil, Transport and Engineering. An interesting and popular commentary on this

part of the exhibition has been written by Dr. J. P. Lawrie and this forms the second part of the handbook.

It is difficult in the compass of this article to do justice to the numerous exhibits, but in the following paragraphs some indication is given of the contents of each section.

The Properties of Gases.—The historical section of the Exhibition begins, appropriately enough, with some of the apparatus used by Thomas Graham, first President of the Chemical Society, in his researches which preceded the enunciation of the laws governing the diffusion of gases. This leads to a series of exhibits illustrating the discovery of the rare gases, which is traced back to Cavendish's experiment, carried out in 1785, by which he showed that air contained one-eightyfifth part by volume of a gas which could not be made to combine with oxygen, or nitrogen, when electric sparks were passed through it. A number of the original spectrum tubes and apparatus are shown, and the visitor may compare the colours given out by pressing a button which lights a series of discharge tubes each containing one of the rare gases. Ramsay and Whytlaw-Gray's microbalance, with which the atomic weight of helium was determined by weighing less than one cubic millimetre of the gas, is a fascinating example of detailed painstaking experimental work. Included also in this section are examples illustrating the development of the liquefaction of gases. Some of Faraday's apparatus and specimens, kindly lent by the Royal Institution, are shown.

The Solid State.—In this section is to be found a series of exhibits to illustrate the development of theories in crystallography and something of the apparatus used by the pioneers. One of the most interesting is a series of letters between Sir William and Sir Lawrence Bragg describing developments in X-ray crystal analysis. A comprehensive collection of crystal structure models of both early and later work is shown.

Colloid Science and Surface Chemistry.—The development is traced back to Faraday and to Graham. Gold films prepared by Faraday are shown, and the Dialysis Bowl of Graham is a reminder of the simple nature of the apparatus in use a century ago. Tyndall's investigations of the scattering of light by colloidal suspensions and his original "Blue-Sky" tube are shown, together with his broth solutions sealed over sixty years ago during his studies on putrefaction by air-borne bacteria.

Liquids and Solutions.—Graham was the pioneer in this field also and his work is illustrated by his liquid diffusion cells. The electrolysis apparatus and standard cell of Faraday are also shown.

Among the exhibits on the application of theory mention may be made of the beautiful collection of early electrotypes and the interesting series of exhibits on metallic corrosion.

Chemical Reactions.—This section, which opens with Cavendish's Eudiometer lent by the University of Manchester, and the apparatus with which Faraday observed, and made use of, the catalytic effect of platinum, is brought up to date with demonstrations of the more modern work on chain reactions, polymerisation processes, etc., leading to the formation of polythene and other plastics. Of particular interest is a small section exhibiting terylene, the promising new British synthetic fibre. An interesting exhibit is made of the history of photography, which is traced from Fox Talbot to the cyanine dyes, while a fine series of Dixon's flame photographs are also included.

Valency and Atomic Structure.—The British contributions in this field are illustrated by, among other items, Newland's Table of the Elements, Moseley's Apparatus, Bohr-Rutherford atomic models, and specimens of organo-metallic derivatives prepared by Sir Edward Frankland and Sir Gilbert Morgan.

Inorganic Chemistry.—It is in this direction that the Chemical Industry was first developed in this country and exhibits include the production of alum, the extraction and refining of precious metals, the production of nickel and glass, and the application of fluorescent substances to lighting, dyestuffs and other problems. On the side of pure research, some apparatus and manuscripts of John Dalton are on view, together with original preparations of Crookes' thallium compounds and specimens illustrating the work of Roscoe on vanadium. A small exhibit also deals with metallurgy, from Faraday's steels to the development of stainless steel cutlery, while the pioneer work of Lawes and Gilbert in agricultural chemistry is also illustrated.

Organic Chemistry.—The work of the organic chemist is represented by a variety of models, apparatus, and specimens to illustrate the vast growth of knowledge of this subject over the past hundred years. Space forbids an adequate description of this important section, but structural theories, carbohydrates, oils and fats, hormones, alkaloids and vitamins, synthetic drugs and chemotherapeutic agents are all well represented by means of charts describing the chemistry involved and showing samples of some of the first preparations made. An attractive display is made of the wide variety of dyestuffs developed in this country, from Perkin's "mauve" to modern work on the phthalocyanines.

Analytical Methods.—The historical section concludes with a

short display of those analytical methods largely developed in Britain. Among those included are gas and water analysis, hydrometry, Marsh's test for arsenic, and records illustrating the analytical applications of spectrography.

Chemistry in Everyday Life.—This part of the exhibition is designed to show the many ramifications of chemistry in our daily life. As an introduction, something is shown of the raw materials with which the chemist works. The inorganic materials and minerals in limited supply are compared to capital. Organic materials derived from plants and animals are the income with which the chemist has to work.

A series of illuminated screens illustrate the operations and processes by which the raw materials of the laboratory are turned into finished products. The visitor is directed through various sub-sections dealing with the main headings under which chemistry affects us all. Our food requires fertilisers and vitamins. Our health is protected by drugs, DDT, penicillin, sewage control, to select a few random examples. The impact of chemistry on building, on fuels, and on transport will be common knowledge to the chemist. But the public will find much to interest them in the exhibits on textiles, plastics, paint, lubricating oils and metallurgy, to name but a few of the more obvious.

Miscellanea

The honours list published on the occasion of H.M. the King's birthday included the following: *Baron:* Sir Roy Lister Robinson, chairman of the Forestry Commission. *C.H.:* J. W. Robertson Scott, author, founder, and until recently editor of *The Countryman*. *D.B.E.:* Miss Caroline Haslett. *Knights:* Dr. W. N. East, for services to the study of criminal psychology; R. R. Enfield, chief economic adviser, Ministry of Agriculture and Fisheries; Prof. D. D. Henderson, professor of psychiatry, University of Edinburgh; Prof. E. L. Kennaway, lately director of the Chester Beatty Research Institute, Royal Cancer Hospital, London; Dr. A. McCance, deputy chairman and joint managing director of Messrs. Colville's, Ltd., Glasgow. *C.B.:* Dr. E. T. Paris, principal director of scientific research (defence), Ministry of Supply. *C.S.I.:* V. K. Maitland, chief conservator of forests, Central Provinces and Berar. *C.M.G.:* R. W. Thornton, agricultural adviser to the High Commissioner for Basutoland, the Bechuanaland Protectorate and Swaziland; R. Watson, director of agriculture, Burma. *C.I.E.:* W. G. Dyson, chief conservator of forests, Madras. *C.B.E.:* J. E. C. Bailey, managing director of Baird & Tatlock, Ltd.; G. L.

Brown, of the National Institute for Medical Research, London; O. F. Brown, assistant secretary, Department of Scientific and Industrial Research; N. S. Clouston, lately commissioner of lands and director of surveys, Nigeria; R. R. Glanville, director of agriculture, Sierra Leone; Dr. J. A. Gunn, director of the Nuffield Institute for Medical Research, University of Oxford; H. L. Kirke, head of the Research Department, B.B.C.; Prof. T. D. J. Leech, dean of the Faculty of Engineering, Auckland University College; J. R. Lumsden, chairman of directors, Highland and Agricultural Society of Scotland; Prof. J. A. Prescott, director of the Waite Agricultural Research Institute and chief of the Division of Soils, Council for Scientific and Industrial Research, Australia; F. A. Secrett, technical adviser on vegetable production, Ministry of Agriculture; J. M. Wordie, for services to exploration in the Antarctic.

Mr. C. R. Attlee has been elected a fellow of the Royal Society under the Statute which provides for the election of persons who either have rendered conspicuous service to the cause of science or are such that their election would be of signal benefit to the Society.

The following have been elected foreign members of the Royal Society: Dr. E. J. Cartan, professor of geometry in the University of Paris and member of the Paris Academy of Sciences; Prof. P. Karrer, professor of chemistry in the University of Zürich; Prof. H. C. Urey, professor of chemistry and director of the Institute for Nuclear Studies, University of Chicago; Dr. Øjvind Winge, of the Carlsberg Laboratory, Copenhagen.

Mr. J. Davidson Pratt, director and secretary of the Association of British Chemical Manufacturers, has been awarded by the American Government the Medal of Freedom with silver palms for his co-operation with the United States while Controller of Chemical Defence Development at the Ministry of Supply during 1940–45.

Sir Alexander Fleming and Sir Howard Florey have each been awarded the Gold Medal of the Royal Society of Medicine for their work on penicillin.

The Council of the Institution of Civil Engineers has awarded the James Alfred Ewing Medal for 1946 to Sir Clifford Paterson, director of the Research Laboratories of the General Electric Co., Ltd., Wembley, for his outstanding contributions to the science of engineering in the field of research.

Other medals awarded include: the Albert Medal of the Royal Society of Arts to Sir Robert Robinson, P.R.S.; the Redwood Medal of the Institute of Petroleum to H. S. Gibson, of the Anglo-Iranian Oil Co., Ltd., Abadan; and those of the Royal Aeronautical Society —Simms Gold Medal: to Prof. L. Aitchison, professor of industrial metallurgy, University of Birmingham; George Taylor (of Australia) Gold Medal: to Prof. A. R. Collar, Sir George White professor of aeronautical engineering, University of Bristol; Wakefield Gold Medal: to Edwin Link, inventor of the "Link trainer"; Society's Silver Medal: to W. G. Carter, chief designer, Gloster Aircraft Co., Ltd.

Mr. F. Brundrett, C.B., has been appointed chief of the Royal Naval Scientific Service in succession to Sir Charles Wright.

Dr. F. N. Woodward, at present director of the Scottish Seaweed Research Association, has been lent to the Department of Scientific and Industrial Research for appointment as director of the United Kingdom Scientific Mission in the British Commonwealth Scientific Office in Washington; he will also act as attaché for scientific questions to the British Embassy in Washington.

The United Kingdom Government has agreed to loan the services of Mr. A. P. Rowe for one year to the Australian Government for the purpose of establishing a Defence Scientific Advisory Committee.

Dr. D. W. Logan has been appointed to succeed Mr. H. Claughton next year as principal of the University of London.

We have noted with great regret the announcements of the death of the following scientific workers during the past quarter: Mr. B. Hilton Barrett, lecturer in geology in the University of Glasgow; Sir Thomas Holland, F.R.S., geologist, principal and vice-chancellor of the University of Edinburgh during 1929–44; Sir Frederick Gowland Hopkins, F.R.S.; Prof. G. E. M. Jauncey, professor of physics at Washington University; Prof. H. S. Jennings, emeritus professor of zoology in Johns Hopkins University; Prof. C. A. Kofoid, emeritus professor of zoology in the University of California; Dr. D. E. Lea, reader in radiobiology in the University of Cambridge; Prof. G. Matthai, emeritus professor of zoology in the University of the Punjab; Prof. N. Morris, regius professor of materia medica and therapeutics in the University of Glasgow; Dr. W. H. Osgood, emeritus curator of zoology in the Field Museum of Natural History; Dr. J. Parkinson, geologist; Dr. Leopold von Portheim, formerly director of the Biological Research Institute of the Academy of

Science in Vienna; Prof. W. Rogowski, professor of electrotechnics at the Technical High School, Aachen; Prof. A. F. Bernard Shaw, professor of pathology in the University of Durham; Prof. A. W. Stewart, formerly professor of chemistry in Queen's University, Belfast; Sir Almroth Wright, F.R.S.

The Astronomer Royal has given an authoritative account of the history of the discovery of the planet Neptune in a little monograph published by the Cambridge University Press (*John Couch Adams and the Discovery of Neptune*, pp. 43, with frontispiece and facsimiles of two of Adams' memoranda. Price 2*s*. net.).

Adams first resolved to tackle this problem on July 3, 1841, for a memorandum, bearing that date, found among his papers after his death read as follows: "Formed a design . . . of investigating, as soon as possible after taking my degree, the irregularities in the motion of Uranus, which are yet unaccounted for; in order to find whether they may be attributed to the action of an undiscovered planet beyond it. . . ." Another possible cause was that the law of gravitation might not hold exactly at great distances, and it was Adams' failure to answer an enquiry from Airy bearing on this point that led Airy to ignore a summary of Adams' work which the latter sent to him. In fact Adams completed his calculation in the long vacation of the year 1845, and in September gave Challis a paper in which the elements of the planet, its mass and its position on October 1, 1845, had been worked out. This calculated position was within 2° of the actual position on that date and a careful search, which Challis might have made, would have led to the discovery of the planet. Le Verrier, at the instigation of Arago, started work on the problem in the summer of 1845 and, in a paper presented to the French Academy in June 1846, concluded that the irregularities in the motion of Uranus must be due to another planet, whose position at the beginning of the year 1847 he calculated. Now convinced that the planet must exist, Airy gave Challis directions for carrying out a search with the Northumberland telescope in the Observatory at Cambridge. Challis made the search in a very perfunctory manner in late July and early August 1846, and failed to recognise it. Meanwhile, Le Verrier had written to Galle, the Astronomer at the Berlin Observatory, and the latter, assisted by D'Arrest, a keen voluntary worker in the Observatory, discovered the planet on September 23, 1846. There are many points of interest in the story told by the Astronomer Royal, who concludes his most interesting monograph with an account of the squabble over the name of the planet.

The U.S. Bureau of Standards published in the *Journal of Research* for January, 1947, a paper called the "Properties of Water-Repellent Fabrics," by John W. Rowen and Domenick Gagliardi. The paper reviews past work and attempts to put this rather vague subject on a fully scientific basis.

Confusion has arisen in the past between the terms "waterproof" and "water-repellent" as applied to garments. A waterproof material is defined as a fabric in which the open spaces between the fibres have been completely filled, resulting in a continuous surface, with consequent negligible air permeability. A water-repellent material, on the other hand, has not had the pores filled, although the surface has usually been treated. Thus the latter material, with which this paper deals, is permeable to air and water vapour, resulting in far greater comfort to the wearer. The extent to which such a material can resist wetting depends mainly on the chemical treatment of the surface, its roughness and porosity, and also upon the possible presence of impurities on the surface.

The various shapes that a drop of water will assume when placed on different surfaces have a great bearing on this subject. If the angle of contact is large (greater than 90°) the drop approximates to a sphere and will not easily wet the surface. When the angle of contact is small (less than 90°) the drop tends to spread over the surface and wet it. An expression is calculated in the paper for the "Work of Adhesion" in terms of the surface tension and the angle of contact, and it is shown that, as the angle of contact increases, the work of adhesion decreases, and consequently the ability of the liquid to wet the surface also decreases. This theory was extended to take into account the size and spacing of the fibres in an actual fabric.

Untreated fibres are usually easily wetted and to make them water-repellent they must be treated with compounds mainly consisting of waxes, petroleum-like molecules and soaps of polyvalent metals.

After due consideration of the variables involved, it might be thought possible to write down a prescription for the optimum conditions, choosing a suitable fabric and treating it to give a high angle of contact to drops of water. Unfortunately this has not been tried, as the present methods of treating fabrics do not guarantee a complete coating to every fibre. Many of the intertwined fibres are left uncoated and the resistance to wetting is accordingly reduced.

Many different methods of testing fabrics have been devised; in fact, there are almost as many methods as there are laboratories

working on the subject. It is rather surprising that no correlation appears to have been attempted between the results of laboratory tests and the performance of the fabrics in the rain, and also that the effect of temperature has not been considered in many of the methods.

The methods of testing the fabrics fall into four main classes: the measurement of the pressure required to force water through the fabric, the wetting and penetration by falling drops, the absorption of water and lastly the measurement of the angle of contact. No one method is alone sufficient to test all the properties of a fabric and a combination of methods is required. The drop-penetration method is particularly useful in predicting the relative performances of different fabrics, showing up differences not revealed by other tests. The paper includes the results obtained when these tests were made, by the authors of the paper, on eleven different raincoat fabrics and four fabrics used by the army.

In the drop-penetration method already mentioned, the time to collect 10 ml. of water passing through the particular specimen is measured. This method has been modified and instead the rate of penetration is measured and plotted against time. The curves obtained for different fabrics all show the same features and are particularly characteristic of this type of material. They each have an initial induction period, followed by an ∫-shaped portion where the rate of penetration increases to a final steady value. They point the way to future improvements, the objects being to make the initial induction period as long and the final rate of penetration as small as possible. This was achieved to a large extent by the American Army during the war when they developed the Shirley type of cloth.

The paper deals finally with the effects that cleaning and laundering have upon fabrics, and a table of results is included in the paper. The extent by which the water-repellent properties of a material are reduced indicates its durability. This reduction is mainly attributed to the leaching of the chemicals with which the fibres have been treated, to residual soap left in the fibres and also to distortion of the fabric structure.

The first part of the *Journal of Research* for February 1947 is devoted to three papers on the concentration of the isotopes of potassium and also of chlorine by means of the countercurrent electro-migration method. The papers deal fully with the theoretical as well as the practical aspects of the subject.

Isotopes are atoms of an element which have different atomic

masses, but the same chemical properties. This method for their separation depends upon the slightly different mobilities that their ions have in an electrolyte formed by dissolving one of their chemical compounds in water. By setting up a steady flow of the electrolyte through a packed column in a direction opposed to the flow of the isotopic ions and at a rate lying between the velocities of these ions, the ions are separated. Thus in the case of potassium the faster $^{39}K^+$ ions make headway against the flow of the electrolyte, whilst the slightly slower $^{41}K^+$ ions are carried back. This results in a concentration of $^{39}K^+$ being built up in the cathode compartment. The anode compartment is provided with a spillway to maintain a constant level in the system.

The method might be compared to a possible way of sorting out strong and weak swimmers by making them swim against a tide of such a strength that the strong swimmers would travel forward with respect to the land, while the weak swimmers would lose ground.

The successful use of this method depends upon the establishment of a local as well as an overall balance between the flow of electrolyte in one direction and the flow of ions in the opposite direction. To reach such a balance it is necessary to conduct the electrolysis through a packing of uniform porosity or through a capillary tube. By this means it is possible to reduce the remixing and back diffusion in the cell. It is also necessary to set very fine limits on the allowable variations in the porosity of the packing, the temperature across the packing (temperature variations would cause convection currents), the potential across the packing and also in the stream flow. Packings made of fine sand proved to be superior to those made of sintered glass, glass wool, asbestos or glass capillary tubes.

To maintain the strength of the electrolyte at a constant value, it is necessary to add reagents at the anode and cathode during the process. Using potassium sulphate as the electrolyte for the separation of the potassium isotopes, sulphuric acid must be added at the cathode and potassium hydroxide at the anode, their concentrations being adjusted to the transport numbers of the respective cation and anion. The electrode reactions involved are $2K^+ + H_2SO_4 = K_2SO_4 + H_2$ at the cathode, and $SO_4^{--} + 2KOH = K_2SO_4 + H_2O + \frac{1}{2}O_2$ at the anode. The liquids are added by means of carefully prepared droppers, whose ends have been ground flat to ensure a constant size of drop. Methyl red is used as an indicator, the liquids being added at such a rate that the liquid in the electrode compartments changes colour between drops. The electrodes themselves consisted of platinum gauze, the potential

applied varying between 200 volts d.c. and 2000 volts d.c. for different experimental arrangements. The cell was kept in a bath to avoid any sudden changes in temperature.

In this method it is necessary to maintain conditions of reflux balance over long periods of time, and while this can be done satisfactorily by manual control, an automatic system has obvious advantages. In potassium cells the pH of the cathode solution proved to be a reliable and sensitive indication of reflux balance and the rate at which acid is added to the cathode compartment is an efficient means of controlling the reflux rate. The pH is indicated by the E.M.F. across two electrodes let into the cathode compartment. This E.M.F. is amplified and made to operate a valve in the acid supply line, the valve opening each time the pH reaches a certain value.

As a result of a series of experiments in which there were small changes in conditions, it was found possible in the case of potassium to raise the abundance ratio $N = {}^{39}K/{}^{41}K$ from its normal value of 14·2 to a maximum value of 24. This ratio was measured by means of a mass spectrometer.

A similar method was employed by Madorsky and Straus to concentrate the isotopes of chlorine. The electrolyte employed was a solution of sodium chloride, and the operation was regulated by means of a stationary boundary between solutions of sodium hydroxide and sodium chloride. The concentration of ${}^{35}Cl$ obtained was 80·7 per cent. compared to the normal value of 75·76 per cent.

ESSAY REVIEW

SCIENCE AND LIFE. By PROFESSOR WILLIAM WILSON, Ph.D., D.Sc. F.R.S. Being a Review of **Science and Life in the World, Vol. I: Science and Civilization. The Future of Atomic Energy; Vol. II: Transportation—A Measurement of Civilization. Light, Life and Man; Vol. III: A Challenge to the World.** The George Westinghouse Centennial Forum, May 16, 17 and 18, 1946. [Vol. I: pp. x + 152, with 11 plates; Vol. II: pp. x + 236, with 12 plates; Vol. III: pp. x + 198, with 28 plates.] (New York and London: McGraw-Hill Book Co., Inc., 1946. 12*s*. 6*d*. each volume.)

JUST a year ago a number of scientists and technologists assembled in Pittsburgh, U.S.A., to celebrate the centenary of the birth of the distinguished American engineer, George Westinghouse. The addresses delivered on that occasion have now been published, in three volumes, with the title *Science and Life in the World*. They constitute an illuminating commentary on the present state of affairs in the world.

Every reader of these addresses must, like the present reviewer, be impressed by the note of grave warning which runs through many of them; sometimes indeed it sinks to one of deep gloom, and sometimes it rises just sufficiently to constitute an expression of *faith* in the future of humanity and human society. Professor A. V. Hill, lately Foreign Secretary and Vice-President of the Royal Society, who delivered the first address (on Scientific Ethics) says "The time is now urgent and the world situation brooks no delay." The gravity of some of the statements of Professor Harold Urey, a distinguished chemist and Nobel Laureate, is even more impressive. He observes that he could tell us of the great benefits which physical science has brought to man, but he continues, "I am *the apostle of doom*" [the present writer's italics]. "I am still a frightened man and I wish you to be frightened." (Vol. iii, p. 126.) After referring to the things with the aid of which mankind can be given "a material and intellectual existence on a level that has never before been known," he adds, "we have brought this civilisation to the very brink of a precipice." These are, of course, no foolishly alarmist statements. The evidence for the state of affairs which has evoked them stares every one in the face.

Dr. Bowman, of Johns Hopkins University, in an address on the Social Composition of Scientific Power, perhaps the finest of them all, says, "We are at this appalling juncture to-day in a world afflicted with a high fever of unrest." Professor Oppenheimer,

speaking about "A Future for Atomic Weapons," is careful to supplement his remarks by the sentence, "If any great note of confidence or gaiety has invested these brief words, it would be a distortion of the spirit in which I should have wished to speak to you." Professor Fermi, whom we in England regard as one of the most outstanding men of science of the present time, refers, in his address on "Atomic Energy for Power," to the "relatively short time that will elapse before the 'secrets' will naturally become open knowledge . . ."

It is impossible, in the space which can reasonably be placed at a reviewer's disposal, to do full justice to the many addresses delivered at the Centennial Forum; but the following addresses should be noted, in addition to those already mentioned, as of special interest and instructiveness: "Nuclear Science in Chemistry," by Dr. H. S. Taylor of Princeton; "Ships and Shipping," by Vice-Admiral E. S. Land; "The Microbe, Friend and Enemy of Man," by Dr. S. A. Waksman; "The Golden Age of the Future," by Mr. A. W. Robertson; and "Scientific Progress," by Dr. Karl Compton.

Some of the addresses are of outstanding value and it is desirable that they should be widely read. No apology need be made for giving more quotations from them. Professor A. V. Hill says: "The truest form of realism to-day is to recognise that human well-being, indeed the continued existence of human society, and any hope at all of reaching the promised land of healthy, orderly development, depend far more on improvements of morality, honesty, tolerance, reasonableness and good faith than on inventions or organisation." He hopes that a Hippocratic Oath may be adopted or that "ethical behaviour in science may just come to be accepted as an honourable obligation as unbreakable as that of accuracy and integrity." Dr. Bowman describes in a few sentences the two extremes in political and social outlook, that of America on the one hand and that of Soviet Russia on the other: "We think that the ultimate loyalties of men are best called out by a system of free enterprise. The Soviet Union believes in a contrary view, and we ask whether the cry of 'encirclement' therefore is an artificial one in the designs of the Soviet leaders, who thus prolong among their people the fear of war?" and he makes the further very striking observation which our politicians, of both parties, here in England, might profitably study: "At a stroke the lessons of man's long creative experiment in social living are by-passed by stigmatising them as the record of capitalism, a charge that some find easy to believe because something is wrong . . ." Then he administers a

sharp correction to the thoughtlessly optimistic enthusiasts who are going to cure the world with science: "Clearly civilisation means something that science can support and amplify, but, *equally clearly* [the present writer's italics] science played but a small part in what was once an acceptable civilisation." Civilisation "does not mean blind power, fortified by science, or power cunningly contrived to keep men bound to a system of work and government that makes the individual the subservient tool of a small group at the top."

Amid the laudatory references to the inventive genius of George Westinghouse and glowing descriptions of the future applications of science and technology—in which transport, in its various forms, and the utilisation of atomic energy are prominent—there is a clear recognition—as indeed one might expect in the land of Ralph Waldo Emerson and David Thoreau—that civilisation is not merely an affair of machines, that certain values, already appreciated in ancient Hellas, are even more important in a good civilisation. Indeed, it may be said that the greatest value of science itself lies quite outside its sphere of practical application—great as its beneficence can be, when rightly applied, with Dr. Hill's Hippocratic spirit. The study of science and the pursuit of scientific enquiry have a value in themselves that is not inferior to that which is associated with their beneficent application. "False indeed," writes Dr. John Baker,* "is the idea that things can only attract the study of human beings if they are of immediate material use." To quote Dr. Bowman once more: "The major achievements of science have in them the stuff of poetry."

Meanwhile, the cloud, which overshadowed the Forum, overshadows the "civilised" world and the urgent question for us is, What can we do *now* and in the immediate future? We are confronted with an emergency which probably will not wait till the general ethical level of humanity rises to that of a universal Hippocratic oath. There seems to be no solution that is universally acceptable. We shall just have to make the best of common sense. As Vice-Admiral Land puts it, in a concluding sentence of his address: "The Atomic Age will not dispense with 'horse sense.'"

* *The Scientific Life*, p. 105 (George Allen & Unwin).

REVIEWS

MATHEMATICS

An Index of Mathematical Tables. By A. FLETCHER,* M.A., Ph.D., J. C. P. MILLER, M.A., Ph.D., and L. ROSENHEAD, Ph.D., D.Sc. [Pp. viii + 451.] (London: Scientific Computing Service, Ltd., 1946, 75*s*. net.)

THIS book provides a detailed and systematic list of references to mathematical tables. In defining the domain of tables to be covered by this index the authors have deliberately omitted specialised tables in the theory of numbers and groups, certain statistical tables and most physical, geophysical and astronomical tables. Further, tables which are only of historical interest as well as those only of limited interest have been excluded. Some 2000 items have qualified for inclusion out of a total of some 3000 references actually compiled.

The book is arranged in two parts, *viz.* a subject index (Part I) and a bibliography (Part II). In the former all tables are classified according to the function tabulated, irrespective of the place of publication. For instance, the tabulation of sin x given in Table VIII of the "Standard Four Figure Tables" (by Milne Thomson and Comrie) is listed in "Section" 7 (Natural Trigonometrical Functions, Miscellaneous functions connected with the circle and the sphere) where it occurs in "Article" 7.41 (Sin x, Degrees, Minutes, etc.), whilst that of log sin x, which in the "Standard Four Figure Tables" is given alongside with sin x, is listed in section 8 (Logarithms of Trigonometrical Functions) where it occurs in the corresponding article 8.41 (Log Sin x, Degrees, Minutes, etc.), and the table of erf(x) from the same book of tables is listed in Section 15 (The Error Integral, etc.), under article 15.211 which is headed

$$\mathrm{H}(x) = 2\pi^{-\frac{1}{2}} \int_0^x \exp.\,(-t^2)dt.$$

Here it is joined with all other references concerning this particular function, starting with Burgess 20 decimal table of H(x) and ending with references to various journals and books of tables where 4-decimal values of this function are given.

There are 24 main sections, each dealing with a class of functions and each comprising a varying number of articles arranged in a logical decimal notation, whilst each of the articles is concerned with a particular function. An "Index to Part I" guides the reader from the name of the function or the type of mathematical formula for which he requires a table to the appropriate article. Should he be unable to find here the required decimal accuracy or argument of the function, he will note in neighbouring articles references to related functions to which his problem might be transformed; there are also excellent cross-references to other sections, based often on a thorough mathematical study of the tables.

Each reference occupies only one or two lines, and, with the help of an admirable short-cut notation, information is given on: Decimal accuracy, range of argument, method of interpolation for which provision is made (*e.g.* the differences tabulated), brief references to errors and to places

corrections might be found and, finally, the link with the bibliographical reference is made by quoting the author's name and the date of publication. This must then be looked up in the alphabetical bibliography of Part II, where the complete reference to book or journal will be found. This Part II of the index can, of course, be used independently as an authors' index.

Thus the user will find his way quickly to the appropriate reference. The only disadvantage of this arrangement is that it does not provide a list of contents of any book of tables, a disadvantage that might have been overcome by back-references from Part II to Part I.

The thoroughness of this exacting, gigantic task of compilation and the high standard of presentation have resulted in a book of reference that should be indispensable to all concerned with numerical mathematics. For the research worker who does not realise that the function he requires has already been tabulated in some obscure journal, this index may save months of drudgery; for the expert who is vexed by the variety of notation used by mathematicians it will act as an infallible interpreter.

We are confident that the authors and publisher will deal with the difficult task of keeping this index up to date in times to come.

H. O. HARTLEY.

Introduction to Mathematical Statistics. By PAUL G. HOEL. [Pp. x + 258, with 35 figures.] (New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd., 1947. 21*s*. net.)

THIS is an attractively produced, well-printed text-book. It is more or less of the usual American type, but there are several interesting innovations. The most interesting of these is the use *ab initio* of moment generating functions. This is a novel feature in a text-book of this standard. Its appearance draws attention to an important question in the teaching of the theory of mathematical statistics. Should moment generating functions be used in elementary distribution theory, or should their application be deferred until the mathematics behind them is more fully understood by the student? The author's work provides an effective argument in favour of the first of these two opinions. Some may still consider moment generating functions too sophisticated to be introduced at such an early stage. It is indeed an interesting question, with its roots in the history of the subject reaching back to Laplace, and should repay close study.

The other innovations are more natural developments. They consist of simplified accounts of more recent results of statistical theory than have been included heretofore in text-books of this type. Runs, non-parametric tests, and sequential sampling are among special topics receiving brief consideration. Incidentally, the term "non-parametric," although sanctioned increasingly by usage, seems to be a misnomer. Non-parametric tests are essentially independent of the form of distribution function, but only accidentally independent of population parameters.

The treatment of the special topics, though brief, is in most instances both lucid and interesting. An unfortunate, but important, exception is the theory of testing hypotheses. The author states that he has found it expedient to leave this subject till the end of the book, though logically it should appear much earlier. As a result much of the necessary development is spread out among various chapters of the book, leading to a certain patchiness and lack of coherency.

There is, indeed, a regrettable reluctance to deal with the fundamental problems of statistical inference. These are, admittedly, not easy, but they are of practical, as well as theoretical, importance. A noteworthy instance of this neglect of fundamentals occurs in the introduction of probability theory. This takes the form of a summary of results assumed to have been acquired in "college algebra". The problems involved in the use of probability theory in mathematical statistics receive scant attention.

The absence of discussion of these points is the more unfortunate as it greatly reduces the value of the book to the private student. In other respects, particularly in regard to the provision of numerous exercises to be worked by the student, the book is well suited for private study.

N. L. J.

The Theory of Functions of Real Variables. By LAWRENCE M. GRAVES. [Pp. x + 300, with 12 figures.] (New York and London: McGraw-Hill Book Company, Inc., 1946. 20s. net.)

THE most obvious difference between Newton's calculus and what our undergraduates learn today is in the standard of rigour, which the nineteenth-century theories of irrational numbers and limits made possible. But over a large field in the theory of functions more fundamental changes have occurred, associated with the names of Borel and Lebesgue; their effects are comparable with those brought about in arithmetic by the introduction of irrational numbers. It is arguable that the inspiration of the French school derives from Cantor, and that the new outlook in the theory of functions has carried it to an imaginative plane where the theory of sets is indispensable. There is, on the other hand, a flourishing opposition to Cantorism and also an understandable desire, on the part of those interested in Lebesgue integration as a tool, to get along with as little theory of sets as possible.

One of the aims of this book is to expound the Lebesgue integral so that the important convergence theorems can be proved with the aid of a rudimentary theory of sets and of measure; in this the author follows F. Riesz. The method, in brief, is to admit null sets and to define the Lebesgue integral of a function, if it is the limit almost everywhere of a sequence of step functions, as the limit of the Riemann integrals of the step functions. Measurability of a set is then identified with the integrability of its characteristic function. Those accustomed to the Lebesgue or Caratheodory methods will know that, in virtue of Lusin's theorem, there is no loss of generality in this approach, but there may be loss of something more important, at least to the post-graduate beginner, namely an understanding of why the Lebesgue integral is superior, and what its place is in the larger scheme of analysis made possible by Cantor. Teachers who make the study of Lebesgue measure and integration also the occasion for a deeper study of sets may consider the treatment of sets in this book to be too sketchy and to leave too much, in the realm of subtle ideas, not technique, to the reader.

In addition to the theory of the Lebesgue integral, which occupies about one-third of the book, there is a chapter on Stieltjes integrals, including a proof of Riesz's remarkable theorem on the form of a linear functional in the space of continuous functions. The choice of the remaining material follows no obvious plan. An interesting chapter develops the real numbers from Peano's axioms to the Dedekind section. Considerable space is given to proofs of certain elementary propositions, such as Rolle's and Taylor's

theorems, apparently as a counterblast to the less rigorous texts that survive in the U.S.A. There is also a chapter on uniform convergence, including Weierstrass's non-differentiable function and his theorem on polynomial approximation to a continuous function (Landau's proof). Other chapters deal, in some detail, with implicit functions and with existence theorems for ordinary differential equations.

The book is everywhere readable, and it achieves a consistently high standard of rigour and clarity.

H. K.

A Chapter in the Theory of Numbers. By L. J. MORDELL. [Pp. 31.] (Cambridge: at the University Press, 1947. 1s. 6d. net.)

THE subject of Professor Mordell's inaugural lecture at Cambridge, here published in booklet form, was the indeterminate equation $y^2 = x^3 + k$, and the researches associated with it. These researches, extending from the time of Fermat to the present day, are of great interest and importance. Incidentally, they illustrate the fact that problems in the theory of numbers, which appear very similar, may require entirely different methods for their treatment. Thus V. A. Lebesgue's proof (1869) that the equation $y^2 = x^3 + 7$ has no solution in integers is entirely elementary, whereas Nagell's enumeration of the eight solutions (with y positive) of $y^2 = x^3 + 17$, and his proof (1930) that there are no other solutions, require very much deeper arguments.

No *general* theorem on equations of the form $y^2 = x^3 + k$ was known until the present century, when it was proved that any such equation (with $k \neq 0$) has at most a finite number of solutions in integers. This was one of the deductions from the profound researches of the Norwegian mathematician Axel Thue on rational approximations to algebraic numbers.

Professor Mordell has done a real service, both to professional mathematicians and to all who have an interest in number-theory, by publishing this lecture on a subject to which he has himself made important contributions. The exposition is clear, and the greater part of the lecture will be intelligible to those who have no expert knowledge.

H. D.

Applied Mathematics for Engineers and Physicists. By LOUIS A. PIPES, Ph.D. [Pp. xiv + 618, with 187 figures.] (New York and London: McGraw-Hill Book Co., Inc., 1946. 27s. 6d. net.)

MATHEMATICAL techniques of quite an advanced character have nowadays to be the stock-in-trade of the physicist and the engineer, and the need for wider mathematical training in undergraduate and higher-degree courses in physics and engineering is now generally recognised. One of the obstacles to the provision of such training has been the lack of a suitable text-book. Most available texts are either not primarily concerned with the actual application of mathematical methods to technical problems or are too specialised in their particular field of application.

The present work is designed to meet this need and it must be said it does so with a considerable amount of success. The author, who is attached to the Research and Electronics Division of the Hughes Aircraft Company, has, during the past five years, given a course in applied mathematics at the Graduate School of Engineering of Harvard University, and this book has been developed from lecture notes prepared for this course.

The book opens with a chapter on infinite series, followed by chapters on complex numbers, Fourier series and integrals, linear algebraic equations, determinants and matrices, and linear differential equations with constant coefficients. In the treatment of such equations the author makes extensive use of the Heaviside Operational calculus and the book includes very useful tables of Laplace transforms. Applications are made to the differential equations occurring in the theory of linear circuits, elastic vibrations of systems with a finite number of degrees of freedom, and elastic beams and columns.

Further chapters deal with the calculus of finite differences, partial differentiation, Gamma, Beta and Error functions, Bessel functions, Legendre Polynomials, Laplace's equation, the diffusion equation, and the wave equation. After a very condensed chapter on vector calculus, the book concludes with an elementary account of functions of a complex variable and a chapter on non-linear oscillatory systems.

Naturally, in a book of this scope, rigour has had to be sacrificed somewhat, but this is compensated for by an adequate bibliography.

The exposition is very lucid throughout and the book is produced in an attractive format.

Although the specific applications of the mathematical techniques are more to problems of engineering than to those of modern physics, this book should prove valuable to advanced students of physics and engineering, to research workers in physics and to professional engineers as well.

E. H. S. B.

ASTRONOMY

Atoms, Stars and Nebulæ. By L. Goldberg and L. H. Aller. Harvard Books on Astronomy. [Pp. vi + 323, with frontispiece and 150 figures.] (U.S.A.: The Blakiston Company; London: J. & A. Churchill, Ltd., 1946. 18*s*. net.)

Readers of the series of the Harvard Books on Astronomy will have become accustomed to finding in them authoritative and up-to-date accounts of various specialised branches of astronomy and astrophysics. There can be little doubt that stellar spectroscopy has made some of the most spectacular contributions to these sciences, both as regards practical techniques and theoretical interpretation. The volume under review is a most successful description of such developments, fully illustrated alike with the stellar and nebular spectra that have been the objects of study as with the portraits of astronomers who have been responsible for many outstanding discoveries. It should not make difficult reading for the student or for the intelligent layman, while the specialist will find in it a most useful summary of current ideas.

Beginning with a description of the astronomer's methods of measuring stellar distances, magnitudes, temperatures, masses and radii, and an outline of the interpretation of atomic and molecular spectra, the reader is taken through the various specialised subjects of the analysis of conditions in a normal stellar atmosphere, in variable or explosive stars, in extensive atmospheres or planetary nebulæ surrounding stellar nuclei, and the peculiar conditions obtaining in interstellar space—now known to contain highly significant quantities of gas and "dust." A final chapter deals with the crucial problems of stellar energy generation and evolution, including of course a useful section on the theories of Bethe and Gamow.

The authors seem to have struck a happy compromise in imparting an occasional light touch to their style, without wandering from technical accuracy. They are usually at pains to define unfamiliar terms and it is all the more surprising that they have not attempted a precise definition of the title-word "nebulæ"; application of this term to external galaxies, however, is strictly avoided and it should be clear that its use is restricted to the detectable aggregations of interstellar and circumstellar material. The rapidity with which the subject advances is underlined when one reads (p. 95) that "the Zeeman splitting of lines has never been observed in stellar spectra"—a statement which will doubtless be modified in a later edition.

A. D. T.

PHYSICS

College Technical Physics. By Robert L. Weber, Marsh W. White, and Kenneth V. Manning. [Pp. x + 761, with frontispiece, 50 portrait drawings and 428 figures.] (New York and London: McGraw-Hill Book Co., Inc., 1947. 22*s*. 6*d*. net.)

This book, the authors of which are all of the Pennsylvania State College, embraces all the main branches of physics treated by elementary mathematics, without the calculus. Numerous solved problems appear, stress being given to the insertion of all units and the proper use of significant figures. Both British and Metric systems of units are employed, each chapter summary being followed by both discussion and numerical questions.

One-third of the book is devoted to the basic principles of statics, dynamics and the fundamentals of fluid and vibratory motion; the heat section is confined to those elements of the subject necessary for the heat engineer. The liberal use of excellent coloured plates in the section on colour clearly brings out, for example, the effects of mixing lights or pigments, whilst the practical approach to electricity and magnetism will be of general appeal to the engineer. The inclusion of chapters on meteorology, building acoustics, interference, polarisation, electronics and nuclear physics is a welcome addition to the stereotyped contents of the ordinary text-book.

On the whole, the book is designed to appeal in particular to all engineering students, emphasis throughout being on the everyday applications of physics. Explanatory photographs of those precision instruments which are not usually available in the laboratory are a feature of this well-illustrated book. Portrait drawings of Nobel prize-winners appear as headpieces to the fifty chapters, followed by brief biographical notes and reasons for the awards. In conclusion, a study of the intriguing "Map of Physics" in the frontispiece gives a delightful picture of how the extension of our knowledge of physics came about.

Cyril Dodd.

Physical Science in Art and Industry. By E. G. Richardson, B.A., Ph.D., D.Sc. Second edition. [Pp. xii + 299, with 77 figures, including 7 plates.] (London: The English Universities Press Ltd., 1946. 15*s*. net.)

The scope of this interesting book can perhaps best be given by a summary of the chapter headings: The Physics of Locomotion (three chapters: vehicles, ships and aeroplanes), Communication Physics (mainly telegraph and telephone), Pottery, Culinary Arts, On the Farm, River Hydrology,

Down the Mine, In Fine Art and Archæology, Building Materials, Architectural Physics, Science and the Musician, Textile Physics, the Physics of Detection (of objects, not criminals !). As Dr. Richardson truly says, physicists working in one industry have often little knowledge of problems being solved by their colleagues in other industries, and this book is of value in showing how frequently a tool or method devised for one investigation may be used with little or no modification in quite a different field.

For proper understanding of the contents of this book, a knowledge of physics to Intermediate standard or beyond is really necessary, but readers without this knowledge could still, with some judicious skipping, read the book with interest and profit. The last chapter has been re-written for this edition and could, with advantage, be expanded in the next. The few slips and inaccuracies which remain are too trivial to be listed here. The book is well printed and the price is reasonable by present standards.

F. A. V.

Die Geschichte der Atombombe (The History of the Atom Bomb). By Hans Thirring. [Pp. 150, with 17 figures.] (Vienna: "Neues Österreich" Zeitungs- und Verlagsgesellschaft m.b.H., 1946.)

Public interest in atomic energy demands popular expositions of this subject in all countries and in all languages, and the book here under review has been written in Austria by a well-known theoretical physicist. Its first part, covering roughly half the book, serves to bring the general reader up to the state of knowledge prior to the discovery of fission.

He succeeds in keeping his language simple and attractive and should be within the reach of the intelligent layman. One drawback of this introduction is that it is entirely restricted to facts, without explaining the methods of investigation by means of which the facts have been ascertained. This will leave the non-expert reader with a feeling of unreality and speculation.

Of the second part, the first three chapters deal with the discovery of fission and its properties. The progress as here described is more logical than was the case historically. The author deduces the existence of secondary neutrons from an *a priori* argument which is not too sound. Next, the problem of realising an atomic chain reaction is discussed, with its difficulties.

Chapter 32 is of particular interest to readers in this country, as it contains the author's views of the reasons why the German project was so utterly unsuccessful. Amongst the reasons he quotes is the influence of Nazi "scientists" opposed to modern physics, the loss of outstanding scientists who had left the country, and the fact that of the remaining men of science some did not wish to see atomic bombs in the hands of the Nazi leaders, others at least were half-hearted about it. Added to those facts was the lack of resources, which probably would have prevented a project on anything like the American scale, even if more progress had been made in the early stages.

Chapters 33 to 38 give the history of the American project, following closely the Smyth Report, from which the information has evidently been taken. Where the account deviates from the Smyth Report, as, for example, in Chapter 39 on the New Mexico test, the description becomes picturesque rather than accurate.

In a brief chapter on the explosions in Japan the question of the moral justification of the atomic bombings is raised. A point made in this connection is of interest, namely that the bombs saved lives not merely by making

an invasion of Japan unnecessary, but also by shortening the war and thus advancing the time when resources became available to deal with the food problems in Europe and to start the fight against starvation there. After pointing out that the " secret " of the atomic bomb is no single secret, but a general body of experience, the book turns to the hypothetical possibility of a super atom bomb in which deuterium is heated to a temperature at which a nuclear reaction starts spontaneously. Of atomic power for peaceful purposes the author is somewhat sceptical. He makes with particular emphasis the point that water power will not be obsolete in the foreseeable future. The last chapter deals with international control, on which the author's views agree closely with those held by scientists in many other countries.

While evidently written for the non-expert reader in Austria, the book is well worth reading even beyond its immediate sphere.

R. E. Peierls.

The Physical Principles of Wave Guide Transmission and Antenna Systems. By W. H. Watson. [Pp. xiv + 207, with frontispiece and 95 figures, including 2 plates.] (Oxford: at the Clarendon Press, 1947. 20*s*. net.)

During the past few years, the extensive use of wave guides in radar and radio equipment has led to the development of a new mathematical technique for dealing with problems associated with bends, twists, slots and obstructions of various kinds in wave guides. Such problems become intolerably complicated when treated by classical methods and the new technique depends upon the simplifying limitation that, for practical reasons, it is usually desirable to choose the size and shape of a wave guide so that there is only one mode by which energy can be propagated. Professor Watson, who has himself made notable contributions to the subject, now gives us, for the first time, a connected account of these and other related matters, and his book will be warmly welcomed by all who are interested in this branch of radio engineering.

Chapter I introduces the necessary fundamental ideas and deals with the application of the concepts of impedance and admittance to plane waves in space. The use of matrices to deal with the resulting algebraic equations is also described. In Chapter II dominant wave propagation in a rectangular guide is presented, while the more general theory of wave guides is reserved for Chapter IV. Chapter III is devoted to a short account of the methods of making measurements on wave guides, but it is doubtful whether this brief summary will be very intelligible to anyone who is not already conversant with the subject. Chapter V introduces the half-wave magnetic radiator and deals with Babinet's Principle and the general methods for treating obstructions and antennas in rectangular guides.

The next three chapters are devoted to the theory of the resonant slot in a rectangular guide and to various applications involving the use of such slots. These chapters contain a great deal of information which is not available elsewhere and are of particular value. Various other devices are discussed in Chapter IX, and Chapter X contains an account of Field Representation.

Throughout the book emphasis is placed on physical principles rather than on mathematical details, and practical applications are kept firmly in view. Although the book is not an easy one to read, the author has done

much to make a highly complicated subject intelligible to the physicist or engineer whose interests are primarily of a practical nature.

The book, which would be improved by the inclusion of a subject index, is one of a series of International Monographs on Radio, under the general editorship of Sir Edward Appleton and Dr. H. G. Booker.

C. W. O.

CHEMISTRY

Fundamentals of Plastics. Edited by H. M. RICHARDSON, B.S., and J. WATSON WILSON, Ph.D. [Pp. viii + 483, with 199 figures and 60 tables.] (New York and London: McGraw-Hill Book Company, Inc., 1946. 25*s*. net.)

THIS book is yet another volume of a general character on the subject of plastics. It is stated to have been compiled from lectures given in U.S.A. during the war with the object of training personnel in plastics technology. It covers four aspects: the relationship of chemical structure to physical properties, six main classes of plastics and high polymers (thermosetting, thermoplastic, rubber-like, polyester and polyamide, cross-linked polymers and silicones), methods of manufacture of products, and evaluation, testing and quality control.

Various authors have contributed, with the usual result that the chapters show great differences in style and presentation, besides being at times repetitive. From the general chemical standpoint, the chapters on vinyl resins and rubber and synthetic elastomers are the most satisfying, although the section on phenolics is pleasingly up to date on the theoretical side. Manufacturing aspects occupy a large proportion of the book; they are well done, but tend to stress compression moulding and its problems at the expense of other methods of fabrication. The testing section, which is good, would be even better if it included more references to methods other than those established and used in U.S.A.

The book suffers in attempting to describe too wide a field in one cover, so that the information given tends to have much more breadth than depth. It could be improved also by stricter editing to avoid overlap, to enlarge the index, to eliminate minor inaccuracies and a fair number of misprints, and to polish the style of writing in some places. Despite these blemishes much of value has been collected together, and workers in the high polymer industry will wish to have the book on their shelves. Even if it contains little that has not appeared in print before, the book will serve as a work of general reference, besides indicating how the progress of plastics is viewed by U.S.A. workers.

N. J. L. M.

The Mechanism of Contact Catalysis. By R. H. GRIFFITH, D.Phil. Second edition. [Pp. xii + 273, with 97 figures.] (London: Oxford University Press, 1946. 21*s*. net.)

THE industrial utility of contact catalysis has resulted in the accumulation of much empirical knowledge about this subject. It is also unfortunately true that, in addition to the differences of interpretation put upon the same results by different investigators, differences of factual observations seem to be more numerous in this field of chemical kinetics than in many others. For

this reason, an author who succeeds in piloting his readers through what is, at first sight, a mass of conflicting and confusing data, and nevertheless contrives to leave them with an understanding of the principles which determine the mechanism of heterogeneous gas reactions, is to be congratulated. Dr. Griffith deserves high praise for the considerable success in this direction which he has achieved in the second edition of his well-known book.

The author's purpose has been to focus attention on the details of the changes taking place at the catalyst-gas interface rather than on the overall kinetics. This aim has dictated an unusual order of presentation. Chapter I is concerned with the preparation, purification and activation of various types of catalyst, Chapter II with adsorption of gases on various potential or actual catalysts, Chapters III and IV with promoters, carriers and poisons, and Chapters V and VI with the surface topography of the catalyst and the physical state of the layer of adsorbed reactant molecules. Only one chapter, (VII), is devoted to the consideration of certain well-investigated processes (notably hydrogenation reactions); and the book concludes with a discussion (Chapter VIII) of the principles now available to guide the selection of the most suitable contact catalyst for a particular reaction.

It is perhaps to be regretted that an account of the transition state approach to heterogeneous reactions has been largely omitted, despite the fact that during the decade between the publication of the two editions this approach, as demonstrated by Eyring and his collaborators, has increased our insight into the mechanism of contact catalysis, to an extent almost comparable with the advance due to experimental studies of spin isomerisation and isotopic exchange reactions. The reason for this omission is probably to be found in the author's statement that the main study is "the catalyst, rather than the reactants." The reviewer also feels that the author has handicapped himself unnecessarily by avoidance of "the fundamental principles of adsorption" (p. 35) because they have been studied by others. A short consideration of the potential energy changes undergone on the approach of an adsorbate molecule to the adsorbent surface, in the manner suggested by Eyring, would have assisted the reader's understanding of the relation between the various types of adsorption, their different rates and heat changes, and the different modes of catalysis to which they give rise. Despite these criticisms, the book is one which can be recommended to students and industrial and research chemists with confidence and is a useful addition to the literature. The type and format conform to the high standards which we have come to expect from the Oxford Press.

F. S. DAINTON.

Advances in Carbohydrate Chemistry, Vol. 2. Edited by W. W. PIGMAN, M. L. WOLFROM and S. PEAT. [Pp. xiv + 323, with frontispiece and 17 figures.] (New York: Academic Press, Inc., 1946. 36*s*. 6*d*. net).

IT is already evident that the *Advances* will not only be read widely, but will be compiled by eminent chemists from all over the world. The authors of this volume, who hail from Canada (2), Great Britain (5) and France (1) in addition to the United States (5) have, in general, maintained the high standard set in the first volume with a series of clear and comprehensive reviews.

It is regrettable that the recent death of Professor H. Hibbert has robbed

us of the anticipation of more articles of the same calibre as his chapter (with Dr. T. H. Evans) on bacterial polysaccharides.

Professor E. L. Hirst and Dr. J. K. N. Jones, like Dr. Emma J. McDonald, have critically surveyed the evidence concerning the chemical structure of certain plant polysaccharides. The former show how the pectins may be regarded as physical mixtures of pectic acid, araban and galactan, while the latter deals with a number of polyfructoses, notably inulin.

In his chapter on mucopolysaccharides and mucoproteins Professor M. Stacey has endeavoured to introduce some order into this complicated field of study. He has devised a system of classification which is based on the protein-carbohydrate ratio, with subdivisions depending on the sugar-building units. Quite naturally, the stress throughout is laid upon the structure of the polysaccharide components rather than the protein moieties.

The first of the promised reviews with an industrial flavour refers to cellulose ethers, which would seem to hold advantages over esters in the plastics field. Suggestions are made for modifying the methods of preparation so that the ethers may be more readily available.

Credit is due to Dr. S. Peat for providing the first adequate summary of the chemistry of anhydro-sugars. He has painted a logical picture, in which a wealth of fact is knitted together with interesting electronic interpretations, clearly indicating the important rôles played by carbonium cations during the formation and scission of anhydro-rings. His colleague, Dr. F. Smith, has lucidly explained how the enolisation and lactonisation of 2-keto and 3-keto acids lead to the production of analogues of ascorbic acid and has related the chemical structures of the products to their physiological activities.

It is a pity that in one paper, concerning the synthesis of hexitols and pentitols, more space is allocated to experimental procedures than to theoretical considerations. The reviewer feels that this should not be so in a publication of this type.

There are two other good articles by Professor C. S. Hudson, and Dr. H. J. Deuel with Dr. M. G. Morehouse, on "Melezitose and Turanose" and "The Interrelation of Carbohydrate and Fat Metabolism."

E. J. Bourne.

Essentials of Petroleum : A Key to Oil Economics. By P. H. Frankel, M.Inst.Pet., M.Inst.F. [Pp. xvi + 173.] (London : Chapman & Hall, Ltd., 1946. 15s. net.)

This little book opens up a new field in petroleum literature. Its general theme is the economics of the oil business in all its phases. As Dr. Egloff points out in his foreword, "it embodies a rather new and unusual treatment of a good deal of contentious and controversial subject matter in connection with petroleum." It is a provocative book and therefore is more than likely to arouse the interest not only of oil-men in particular but of economists in general. Fortunately the author has had the opportunity of studying the day-by-day working of the industry in many countries and, specially, on both sides of the Atlantic, and so he speaks with no little authority. He dwells on the unique fact that petroleum is a liquid and that therefore special problems arise in dealing with it—problems of storage and transport, of pipelines and of tankers—the latter perhaps to be regarded as a "floating pipeline."

The book is divided into five sections :—Oil and Public Opinion, Eco-

nomics of a Liquid, Price Structure, The Shape of the Industry, and Policies for the Industry. Two appendices deal with Transport, Cost and the Price of Motor Spirit, and the Economics of Tanker Shipments.

The author's views on the control of the industry by a few major groups and the international aspect of such control are of considerable interest.

The book is well documented and is provided with a useful bibliography and ample notes and references.

Altogether Dr. Frankel covers much new ground and his work is *sui generis.*

A. E. DUNSTAN.

BIOLOGY AND MEDICINE

Insect Microbiology. By EDWARD A. STEINHAUS. [Pp. xiv + 763, with 250 figures.] (Ithaca, New York: Comstock Publishing Co., Inc.; London: Constable & Co., Ltd., 1946. 45*s*. net.)

As the first comprehensive survey of the varied relations existing between insects and micro-organisms this book will be warmly welcomed. Ever since 1893, when the cattle tick was found by Smith and Kilbourne to be the invertebrate host of the *Babesia* parasite responsible for Texas cattle fever, the rôle of arthropods in transmitting disease-carrying organisms to vertebrates has been the central theme of a series of brilliant advances in medical science. Nevertheless, the urgent development of this subject has in some respects taken place at the expense of our understanding of insect diseases and of the relations between insects and non-pathogenic organisms, interesting and fundamental though these may be. One consequence is that, whereas there are a number of excellent text-books of medical and veterinary entomology, there are very few which treat the symbiotic relations of insects and micro-organisms and none at all on insect microbiology as a whole. This book is, therefore, something more than an able exposition of known facts, a successful stocktaking; it represents in fact a readjustment of perspective within a field which has naturally tended to become increasingly centred about man and his welfare. The proportions of the book, deriving from this wider viewpoint, can be judged from the following random examples. Eleven pages are devoted to the rickettsia of epidemic typhus, six to the mycetomes of the sucking lice; the agents of silkworm jaundice and the yellow fever virus are each assigned four pages; the transmission of plague bacilli is described in five pages, that of *Bacillus popilliæ*, deadly to the Japanese beetle, in two, and so on.

The opening chapter on extracellular bacteria describes associations ranging from the adventitious to the harmonious relations established by insects with bacterial crypts. The second contains an annotated catalogue of specific bacteria associated with insects. There follow three chapters dealing respectively with intracellular bacterium- and rickettsia-like symbionts, with the organisms associated with insects, ticks and mites that have been definitely assigned to the rickettsias, and with the extra- and intracellular yeasts. The arrangement of these sections presents special difficulties, for only too often the nature of a particular micro-organism is unknown. The amount of overlapping has been reduced to a minimum by relegating most of these relationships to the chapter on intracellular symbionts and by arranging the material according to the arthropod host. Particular attention is given here to the biological relationships involved, the

functions of the symbionts, their mode of transmission and the adaptations displayed by the host for their reception. Later chapters are concerned with the fungi, ranging from those forms pathogenic to insects to the fungus gardens cultivated by the ambrosia beetles; with the virus associations, including the wilts and polyhedral diseases of insects as well as the transmission of plant viruses; with the spirochætes; and lastly with the protozoa. A special chapter is reserved for the unique relations of termites with their flagellate fauna.

This bare recital of the contents will convey the scope of this work. As Professor Steinhaus remarks in his Introduction, insect microbiology, besides entomology, embraces the sciences of bacteriology, protozoology, mycology, pathology and immunology. Small wonder perhaps that in the past few have been tempted to paint so broad a canvas! For this very reason, nevertheless, the present volume will earn the thanks of the teacher, the advanced student and the research worker. It remains to add that the bibliography, which extends to over 1600 references, covers much literature published in inaccessible journals. The book is finely produced and the 250 illustrations include a number of excellent original photographs of micro-organisms.

A. D. L.

Bovine Mastitis. A Symposium. Edited by R. B. LITTLE, V.M.D., and W. N. PLASTRIDGE, Ph.D. [Pp. xii + 546 with 70 figures.] (New York and London: McGraw-Hill Book Co., Inc., 1946. 35*s.* net.)

THE magnitude of the dairy industry and the ravages inflicted on it by disease makes the appearance of this book, written by experts in their various fields, particularly valuable. The chapters on the Anatomy of the Udder by M. A. Emmerson, and that on the Physiology of Milk Secretion by C. W. Turner, which give up-to-date information on the structure of the udder, the effect of internal secretions on the growth of the udder and the letting-down of milk, should be useful to dairy students. A well-illustrated chapter on Pathology by L. B. Sholl, and one on the seriological classification of the mastitis streptococci by A. W. Stableforth, are of special interest to the laboratory worker, while the veterinarian should find much useful information in the chapters on Diagnosis, Transmission, Eradication and Treatment. The dairy farmer will also find much of interest in the chapters on Environmental Factors and Stable Hygiene. While work on treatment with sulphanilamide and penicillin is discussed, it is stressed that prevention is the real answer to bovine mastitis. The standard of the book is guaranteed by the fact that the senior author is on the staff of the Rockefeller Institute for Medical Research at Princeton, New Jersey. The book contains an extensive list of references to original papers, scattered over a wide range of publications, and should form a good focal point for research workers and others wishing to obtain an over-all picture of the disease.

J. H.

Functional Anatomy of the Mammal. By W. JAMES LEACH. [Pp. viii + 231, with 96 figures.] (New York and London: McGraw-Hill Book Co., Inc., 1946. 12*s.* 6*d.* net.)

THERE are many students such as nurses and physiotherapists whose curriculum demands some knowledge of human anatomy. They seldom have an

opportunity to dissect the human body or see prepared dissections, and most of their knowledge is gained from text-books, and their pictures and diagrams, and lectures. There are, however, sufficient structural similarities between, for example, the Cat and Man to justify dissection of the former as a guide to the latter. This book is an attempt to provide such a guide.

Approaching the book from the point of view of a student learning anatomy for the first time, it can be said that, after using this book to help in dissecting the Cat, one's knowledge of the anatomy of Man would be frequently very confused. The author fails in many places to point out the main differences between the Cat and Man. For example, the distribution of the cranial nerves as described on pp. 193 and 194 is very misleading, if applied to Man. In addition, much of the information on Man is wrong or difficult to follow. This is especially obvious in the description of the movements at the shoulder joint.

The author also likes to add a certain number of medical details in order, one presumes, to stimulate the interest of the reader. This type of book is not the correct place for such snippets of information, especially if they are factually in doubt. How many medical men would agree with what is given as a possible cause of hernia in female children on p. 100?

There are numerous diagrams throughout the book. Many are open to criticism because they are misleading and inaccurate. For example, p. 4, Fig 1.1, shows a human "tensor fascia lata" (this should be "tensor fasciæ latæ") and "biceps femoris" which are quite wrong. The "blood vessel" depicted on p. 27, Fig. 2.4, should point in the other direction. On p. 56, Fig. 2.24, the caption refers to "P–P" which cannot be found in the diagram.

There are also many printing errors throughout the book, and some sentences are badly written. Words have often more than one spelling; for example "vermis" of the cerebellum is elsewhere "vermes". Although *Dorland's Medical Dictionary* is his source for terminology and pronunciation, the author usually ignores the Latin or Greek basis for many of the terms used. For example, "hallucis" is always referred to as "hallicus"; terms such as "punctum lacrimalis" and "papilla lacrimale" constantly appear; "ostium tubæ" appears twice as "ostium tuba". And yet it is not as if the author were completely indifferent to Latin and Greek. The plural of "plexus" is always referred to as "plexi", which plural of course is quite wrong.

It can be said that a book of this type could serve a useful purpose, but this volume requires rewriting before it can be regarded as satisfactory.

J. Joseph.

Biochemistry of Cancer. By Jesse P. Greenstein. [Pp. viii + 389, with 39 figures.] (New York: Academic Press, Inc., 1947. 43*s*. net.)

Dr. Greenstein is head biochemist at the United States National Institute for Cancer Research and an authority on enzymes in cancer. His book, *Biochemistry of Cancer*, is in fact two books in one. For less than half its length it consists of chapters on cancer-producing factors (138 pages) and nutrition, endocrinology and chemotherapy (in all, 35 pages). The greater part of the book is neither more nor less than a monograph, largely the author's own experimental work, on the enzyme characteristics of tumours and on the enzymic changes in human and animal tissues produced when a tumour is growing in the body. Strictly speaking, the author is justified

in calling this lop-sided arrangement "Biochemistry of Cancer," since biochemistry has predominated in the enzyme and nutrition aspects, while the study of carcinogens has drawn rather more on organic chemistry, and endocrinology on experimental pathology.

This is no humdrum reference book, but a vigorous exposition of what the author considers essential in cancer research. By comparison Stern and Willheim's *Biochemistry of Malignant Tumours* (1943 edition) seems too sober; there enzymes are given 55 out of 885 pages and 274 references from a total of 5000.

After a prodigious display of energy in the attack on the problems of the enzymes in cancer, Greenstein has concluded that:

1. The enzyme systems of tumours resemble each other more than they do those of normal tissues.

2. There is more uniformity between tumours than between normal tissues.

3. "The activity of each enzyme in tumours falls somewhere within the range of that enzyme in normal tissues, sometimes near the upper end of the range, more often near the lower end of the range, but never outside the normal range."

4. "Malignant tissues, in comparison with normal tissues and benign tumours, are characterised not only by possessing the lowest concentration of cytochrome C but also by possessing the greatest disparity between the components of the cytochrome oxidase-cytochrome C system."

5. "Warburg's early prophecy of a deficient respiratory mechanism in tumours has been sustained by the observation of very low amounts of the cytochrome system, of catalase, of the flavin enzymes and of coenzyme in these tissues."

6. The tissues of an animal bearing a tumour show some of the enzymic properties of the tumours, *i.e.* the whole animal is cancerous.

Interesting as conclusion six may be, it would be more acceptable if one allowed for the qualification that the tumour has to be at least 5 per cent. of the total weight of the animal before the enzyme effects become obvious, and that other diseases besides cancer disturb the enzyme picture in the body.

The amount of information briefly surveyed in this work is enormous; nearly a thousand references are catalogued in the bibliographies. Greenstein's method of reporting researches by using tables of data lifted bodily from the most recent and interesting publications often imparts a certain vivid atmosphere to *Biochemistry of Cancer*. Yet the author's facility in being able so expertly to compress full-length papers into summaries imposes a strain on the reader, for a diet so highly concentrated can be comfortably digested only by specialists who would probably prefer to prepare their own card indices for their particular branch of the subject.

The short section headed "The Possibility of Relatively Non-Specific Endogenic Carcinogens," apart from the inelegance of its title, contains some severe criticisms, suggesting that the author is by no means in sympathy with the aims of workers in this field nor is he familiar with their recent original papers.

A somewhat gloomy passage shows that Greenstein is evidently far from satisfied with the progress of the search for the cause and cure: "Somehow or somewhere there is locked within the chemical pattern of the cancer cell the mechanism for autonomous growth. Were this pattern known, the beginning of a rational approach to the systemic control of the cancer cell

could be instituted. The goal would be to insinuate by subtle chemical means an inhibition of the master reactions responsible for unlimited growth and, thus, to use a delicate rapier to master the cancer rather than the bludgeons so far available or suggested. Thus far the efforts described in this chapter to find a unique metabolism for tumours are not yet definite and useful for this purpose. Until this is accomplished the systemic approaches to the control of the cancer cell can have only an empirical quality."

The author has not been able to avoid a few tautologies. There is nothing illuminating in a statement like—"Neoplastic cells arise when, in some as yet unknown manner, the normal exercise of control has been disturbed"; or, "The induction of tumours is a function of exogenous and endogenous factors, as is, in a dependent phase, the growth and maintenance of an established tumour." These passages should have been drastically pruned, for they could have been written twenty-five years ago, and are superfluous in a work bristling with "hot news from the cancer front."

I. H.

MISCELLANEOUS

The Anatomy of Lango Religion and Groups. By T. T. S. HAYLEY, M.A. [Pp. xii + 207, with 13 plates and 2 folders.] (Cambridge: at the University Press, 1947. 21*s*. net.)

THE author, an economist by training, has been much impressed by the fact that a social group struggles hard to ensure its own continuation and blends emotional, economic and intellectual efforts in the attempt to project itself into the future. He here gives results of his experience and studies among the Lango more or less in note form. For the Lango, Jok is a neutral immanent power, neutral to mankind, but usable by men for good or ill. It is the unknown cause of anything unusual or mysterious. Winyo is luck or power within a man, and a slayer will take his victim's headdress and hang it up to add the dead man's "power" to his own and so cause himself to be feared. The diverse types of groups which coexist for different aspects of life are a most complex study, as they would be amongst ourselves, some based on relationship, some on age, some on neighbourhood and some on work. Hayley describes many ceremonies that aim at maintenance of the diverse groupings. He provides on the whole a valuable body of knowledge, with a steady attempt to avoid distortion by introduction of theory. Needless to say, the success in this last effort is partial, as it is in all efforts of the human intellect. There are numerous glimpses of changes brought about among the Lango by contact with missionaries and other influences from modern European life.

H. J. F.

BOOKS RECEIVED

(Publishers are requested to notify prices.)

A Chapter in the Theory of Numbers. By L. J. Mordell, Sadleirian Professor of Pure Mathematics in the University of Cambridge. An Inaugural Lecture. Cambridge: at the University Press, 1947. (Pp. 31.) 1*s*. 6*d*.

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